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(54) Apparatus for spectrometrically measuring isotopic gas

(57) An apparatus for spectrometrically measuring an isotopic gas is adapted to determine concentrations of a plurality of component gases in a gaseous test sample by introducing the gaseous test sample into a cell, then measuring intensity of light transmitted through the gaseous test sample at wavelengths suitable for the respective component gases, and processing data of the light intensity, characterized by gas injection means for sucking therein the gaseous test sample and then injecting the gaseous test sample into the cell by mechanically pushing out the gaseous test sample at a constant rate.

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EP 1 378 743 A2

Description

Technical Field

[0001] The present invention relates to apparatuses for spectrometrically measuring the concentration of an isotopic gas on the basis of a difference in the light absorption characteristics of the isotope.

Background Art

[0002] Isotopic analyses are useful for diagnosis of a disease in a medical application, in which metabolic functions of a living body can be determined by measuring a change in the concentration or concentration ratio of an isotope after administration of a drug containing the isotope. In the other fields, the isotopic analyses are used for studies of the photosynthesis and metabolism of plants, and for ecological tracing in a geochemical application.

[0003] It is generally known that gastric ulcer and gastritis are caused by bacteria called helicobacter pylori (HP) as well as by a stress. If the HP is present in the stomach of a patient, an antibiotic or the like should be administered to the patient for bacteria removal treatment. Therefore, it is indispensable to check if the patient has the HP. The HP has a strong urease activity for decomposing urea into carbon dioxide and ammonia.

[0004] Carbon has isotopes having mass numbers of, 12, 13 and 14, among which ^{13}C having a mass number of 13 is easy to handle because of its non-radioactivity and stability.

[0005] If the concentration of $^{13}CO_2$ (a final metabolic product) or the concentration ratio of $^{13}CO_2$ to $^{12}CO_2$ in breath of a patient is successfully measured after urea labeled with the isotope ^{13}C is administered to the patient, the presence of the HP can be confirmed.

[0006] However, the concentration ratio of $^{13}CO_2$ to $^{12}CO_2$ in naturally occurring carbon dioxide is 1:100. Therefore, it is difficult to determine the concentration ratio in the breath of the patient with high accuracy.

[0007] There have been known methods for determining the concentration ratio of $^{13}CO_2$ to $^{12}CO_2$ by means of infrared spectroscopy (see JPB 61(1986)-42219 and JPB 61(1986)-42220).

[0008] In the method disclosed in JPB 61(1986)-42220, two cells respectively having a long path and a short path are provided, the path lengths of which are adjusted such that the light absorption by $^{13}CO_2$ in one cell is equal to the light absorption by $^{12}CO_2$ in the other cell. Light beams transmitted through the two cells are lead to spectrometric means, in which the light intensities are measured at wavelengths each providing the maximum sensitivity. In accordance with this method, the light absorption ratio can be adjusted to "1" for the concentration ratio of $^{13}CO_2$ to $^{12}CO_2$ in naturally occurring carbon dioxide. If the concentration ratio is changed, the light absorption ratio also changes by the amount of a change in the concentration ratio. Thus, the change in the concentration ratio can be determined by measuring a change in the light absorption ratio.

(A) In a conventional infrared spectrometric method as described above, a bag containing a gaseous sample is connected to a predetermined pipe of a spectrometric apparatus, and the gaseous sample is introduced into a cell through the pipe by manually compressing the bag.

[0009] However; even small turbulence may drastically reduce the measurement accuracy because the absorbance of $^{13}CO_2$ present in a trace amount is measured in the isotopic gas analysis. The gaseous sample cannot be passed through the cell at a constant flow rate by the manual compression of the bag. This generates a nonuniform flow of the gaseous sample in the cell and causes the gaseous sample to have a local temperature change and an incidental concentration change, thereby fluctuating a light detection signal.

[0010] The flow rate of the gaseous sample may be controlled to be constant by using a pump and a flow meter in combination. However, the accuracy of the flow control cannot be ensured, because the volume of the bag containing the gaseous sample is small and the flow rate is low. Alternatively, an apparatus called mass flow meter for electronic flow control may be employed as flow control means. This improves the accuracy of the flow rate control, but results in a complicated apparatus and an increased cost.

Disclosure of the Invention

[0011] It is an object of the present invention to provide an apparatus for spectrometrically measuring an isotopic gas, which has a simple construction and is capable of introducing a gaseous test sample containing a plurality of component gases at a constant flow rate for spectrometry.

[0012] To achieve the aforesaid objects, the present invention provides an apparatus for spectrometrically measuring an isotopic gas, which includes a gas injection means for sucking therein a gaseous sample and then injecting the gaseous sample into a cell by mechanically pushing out the gaseous sample at a constant flow rate (claim 1).

[0013] With this construction, the gaseous sample is injected into the cell at a constant flow rate. Therefore, the gaseous sample uniformly flows within the cell, so that a highly accurate light detection signal free from fluctuation can

be provided for more accurate concentration measurement.

[0014] Usable as the gas injection means for mechanically pushing out the gaseous sample at the constant rate is, for example, a mechanism including a piston and a cylinder and adapted to move the cylinder at a constant rate.

[0015] In accordance with another aspect of the present invention, the apparatus for spectrometrically measuring an isotopic gas further includes a temperature maintaining means for maintaining a cell for receiving the gaseous sample introduced therein at a constant temperature (claim 2).

[0016] By keeping the temperature within the cell constant, the temperature condition of the gaseous sample can be kept uniform, so that a highly accurate light detection signal free from fluctuation can be provided.

[0017] The foregoing and other objects and features of the present invention will become apparent from the following description with reference to the attached drawings.

Brief Description of Drawings

[0018] Hereinafter, concentration of $^{12}CO_2$ is called "^{12}Conc", concentration of $^{13}CO_2$ is called "^{13}Conc", absorbance of $^{12}CO_2$ is called "^{12}Abs" and absorbance of $^{13}CO_2$ is called "^{13}Abs".

Fig. 1 is a graphical representation in which concentrations ^{12}Conc and concentration ratios ^{13}Conc/^{12}Conc are plotted as abscissa and ordinate, respectively, the concentrations ^{12}Conc and ^{13}Conc and the concentration ratios ^{13}Conc/^{12}Conc having been determined by using calibration curves prepared on the basis of measurements of the absorbances ^{12}Abs and ^{13}Abs of component gases in gaseous samples having the same concentration ratio ^{13}Conc/^{12}Conc but different concentrations of the component gases;

Fig. 2 is a graphical representation in which $^{13}CO_2$ concentration ratios are plotted with respect to oxygen contents, the $^{13}CO_2$ concentration ratios having been determined by measuring gaseous samples containing $^{13}CO_2$ diluted with oxygen and nitrogen and having the same $^{13}CO_2$ concentration ratio but different oxygen concentrations, the $^{13}CO_2$ concentration ratios being normalized on the basis of a $^{13}CO_2$ concentration ratio for an oxygen content of 0%;

Fig. 3 is a graphical representation illustrating the result of measurement in which gaseous samples having different $^{13}CO_2$ concentration ratios and containing no oxygen were measured, in which graphical representation the actual $^{13}CO_2$ concentration ratios and the measured $^{13}CO_2$ concentration ratios are plotted as abscissa and ordinate, respectively, and the $^{13}CO_2$ concentration ratios are normalized on the basis of the minimum $^{13}CO_2$ concentration ratio;

Fig. 4 is a graphical representation illustrating the result of measurement in which gaseous samples having different $^{13}CO_2$ concentration ratios and containing various concentration of oxygen (up to 90%) were measured, in which graphical representation the actual $^{13}CO_2$ concentration ratios and the measured $^{13}CO_2$ concentration ratios are plotted as abscissa and ordinate, respectively, and the $^{13}CO_2$ concentration ratios are normalized on the basis of the minimum $^{13}CO_2$ concentration ratio;

Fig. 5 is a view illustrating the appearance of a breath sampling bag to be connected to nozzles of an apparatus for spectrometrically measuring an isotopic gas;

Fig. 6 is a partial view illustrating pipes connected to an end of the breath sampling bag;

Fig. 7 is a block diagram illustrating the overall construction of the spectrometric apparatus;

Fig. 8 is a sectional view illustrating the construction of a cell chamber 11;

Fig. 9 is a block diagram schematically illustrating a mechanism for adjusting the temperature of the cell chamber;

Figs. 10A and 10B are a plan view and a side view, respectively, of a gas injector for quantitatively injecting a gaseous sample;

Fig. 11 is a diagram illustrating a gas flow path through which a clean reference gas is passed for cleaning the gas flow path and the cell chamber of the spectrometric apparatus;

Fig. 12 is a diagram illustrating a gas flow path through which the clean reference gas is passed for cleaning the gas flow path and the cell chamber of the spectrometric apparatus and for performing a reference measurement;

Fig. 13 is a diagram illustrating a state where a base gas is sucked from a breath sampling bag by means of the gas injector 21 with the reference gas prevented from flowing through first and second sample cells 11a and 11b;

Fig. 14 is a diagram illustrating a gas flow path to be employed when the base gas sucked in the gas injector 21 is mechanically pushed out at a constant rate by the gas injector 21 for measurement of light intensity by detection elements 25a and 25b;

Fig. 15 is a diagram illustrating a state where a sample gas is sucked from the breath sampling bag by means of the gas injector 21 with the reference gas prevented from flowing through the first and second sample cells 11a and 11b;

Fig. 16 is a diagram illustrating a gas flow path to be employed when the sample gas sucked in the gas injector 21 is mechanically pushed out at a constant rate by the gas injector 21 for measurement of light intensity by the

detection elements 25a and 25b;

Fig. 17A is a graphical representation in which $^{12}CO_2$ concentrations and $^{12}CO_2$ absorbances are plotted as abscissa and ordinate, respectively, for preparation of a calibration curve, the $^{12}CO_2$ absorbances having been measured for 20 measuring points in a $^{12}CO_2$ concentration range of about 0% to about 6%;

Fig. 17B is a graphical representation in which $^{12}CO_2$ concentrations and $^{12}CO_2$ absorbances in five data points in a relatively narrow $^{12}CO_2$ concentration range around a $^{12}CO_2$ concentration determined by using the calibration curve of Fig. 17A are plotted as abscissa and ordinate, respectively;

Fig. 18A is a graphical representation in which $^{13}CO_2$ concentrations and $^{13}CO_2$ absorbances are plotted as abscissa and ordinate, respectively, for preparation of a calibration curve, the $^{13}CO_2$ absorbances having been measured for 20 measuring points in a $^{13}CO_2$ concentration range of about 0.00% to about 0.07%;

Fig. 18B is a graphical representation in which $^{13}CO_2$ concentrations and $^{13}CO_2$ absorbances in five data points in a relatively narrow $^{13}CO_2$ concentration range around a $^{13}CO_2$ concentration determined by using the calibration curve of Fig. 18A are plotted as abscissa and ordinate, respectively;

Fig. 19 is a graphical representation in which concentration ratios $^{13}Conc/^{12}Conc$ plotted as ordinate are normalized on the basis of a concentration ratio $^{13}Conc/^{12}Conc$ obtained when $^{12}Conc$ is 0.5%;

Fig. 20 is a graphical representation illustrating the relationship of $^{12}Conc$ (plotted as abscissa) versus $^{13}CO_2$ concentration ratio $^{13}Conc/^{12}Conc$ (plotted as ordinate) which was determined by measuring the $^{12}CO_2$ concentrations $^{12}Conc$ and $^{13}CO_2$ concentrations $^{13}Conc$ of gaseous samples;

Fig. 21 is a graphical representation illustrating the relationship of $^{12}Conc$ (plotted as abscissa) versus concentration ratio $^{13}Conc/^{12}Conc$ (plotted as ordinate) which was determined by measuring the $^{12}CO_2$ concentrations $^{12}Conc$ and $^{13}CO_2$ concentrations $^{13}Conc$ of gaseous samples and correcting obtained concentration ratios $^{13}conc/^{12}Conc$;

Fig. 22 is a graphical representation illustrating the relationship of $^{12}Conc$ (plotted as abscissa) versus concentration ratio $^{13}Conc/^{12}Conc$ (plotted as ordinate) which was obtained by determining the $^{12}CO_2$ concentrations $^{12}Conc$ and $^{13}CO_2$ concentrations $^{13}Conc$ of gaseous samples on the basis of absorbances measured on the gaseous samples by using the calibration curves shown in Figs. 17A and 18A;

Fig. 23 is a graphical representation illustrating the relationship of $^{12}Conc$ (plotted as abscissa) and concentration ratio $^{13}Conc/^{12}Conc$ (plotted as ordinate) which was obtained by determining the concentration ratios $^{13}Conc/^{12}Conc$ of gaseous samples first on the basis of the calibration curves shown in Figs. 17A and 18A and then on the basis of the calibration curves in limited ranges shown in Figs. 17B and 18B; and

Fig. 24 is a graphical representation illustrating the result of measurement in which gaseous samples having different $^{13}CO_2$ concentration ratios and containing various concentration of oxygen (up to 90%) were measured and measurements were subjected to a correction process according to the present invention, in which graphical representation the actual $^{13}CO_2$ concentration ratios and the measured $^{13}CO_2$ concentration ratios are plotted as abscissa and ordinate, respectively, and the $^{13}CO_2$ concentration ratios are normalized on the basis of the minimum $^{13}CO_2$ concentration ratio.

Best Mode for Carrying Out the Invention

[0019] A preferred embodiment of the present invention will hereinafter be described with reference to the attached drawings. The embodiment is adapted for a case where a $^{13}CO_2$ concentration or concentration ratio $^{13}Conc/^{12}Conc$ in a breath test sample is spectrometrically determined after administration of an urea diagnostic drug labeled with an isotope ^{13}C.

I. Breath test

[0020] Before the urea diagnostic drug is administered to a patient, breath of the patient is sampled in a breath sampling bag. The volume of the breath sampling bag may be about 250ml. Then, the urea diagnostic drug is administered to the patient and, after a lapse of 10 to 15 minutes, breath of the patient is sampled in the breath sampling bag in the same manner as in the previous breath sampling.

[0021] Fig. 5 is a view illustrating the appearance of the breath sampling bag 1 to be connected to nozzles N_1 and N_2 of an apparatus for spectrometrically measuring an isotopic gas. The breath sampling bag 1 includes a breath sampling chamber 1a for sampling breath of the patient after the administration of the urea diagnostic drug and a breath sampling chamber 1b for sampling breath of the patient before the administration of the urea diagnostic drug, the breath sampling chambers 1a and 1b being integrally molded and joined together to form a single body.

[0022] A pipe 2a is attached to an end of the breath sampling chamber 1a, and a pipe 2b is attached to an end of the breath sampling chamber 1b. Bottom ends 5a and 5b of the breath sampling chambers 1a and 1b are closed. The pipes 2a and 2b each have two functions, i.e., the pipes 2a and 2b serve not only as breath blowing ports from which

breath is blown into the breath sampling chambers 1a and 1b, but also for introducing the breath samples from the breath sampling chambers 1a and 1b into the spectrometric apparatus when the breath sampling bag is connected to the nozzles N_1 and N_2 of the apparatus.

[0023] When breath is sampled, a cylindrical filter (like cigarette filter) 7a or 7b is fitted into the pipe 2a or 2b, and then the breath is blown into the breath sampling bag 1. The filters 7a and 7b are used to remove moisture in the breath.

[0024] As shown in Fig. 6, back-flow valves 3a and 3b are provided in the pipes 2a and 2b, respectively, for preventing the breath blown into the breath sampling bag from flowing back.

[0025] The pipes 2a and 2b each have a portion having a smaller inner diameter (e.g., a smaller diameter portion 4a or 4b) for generating a resistance to the blowing of the breath. The resistance to the blowing of the breath allows the patient to exhale air from his lung. It has been experimentally confirmed that air exhaled from the lung of a patient provides a more stable CO_2 concentration than air present in the oral cavity of the patient.

[0026] After the completion of the sampling of the breath, the filters are removed, and the pipes 2a and 2b are inserted into the nozzles N_1 and N_2, respectively, of the spectrometric apparatus. The nozzles N_1 and N_2 have different inner diameters, and the pipes 2a and 2b have different outer diameters corresponding to the inner diameters of the nozzles N_1 and N_2. This prevents the pipes 2a and 2b from being inserted into wrong nozzles N_2 and N_1, thereby preventing the breath samples obtained before and after the administration of the urea diagnostic drug from being mistakenly manipulated.

[0027] The nozzles N_1 and N_2 of the spectrometric apparatus have projections 6a and 6b, respectively, which are adapted to disable the function of the back-flow valves 3a and 3b when the pipes 2a and 2b are inserted into the nozzles N_1 and N_2.

[0028] Although the outer diameters of the pipes 2a and 2b are made different in this embodiment, any other constructions may be employed to prevent the mistake of connection between the pipes 2a and 2b and the nozzles N_1 and N_2. For example, the pipes may have different lengths and the nozzles N_1 and N_2 of the spectrometric apparatus may have different depths corresponding to the lengths of the pipes. With this construction, a longer one of the pipes mistakenly inserted into a nozzle having a smaller depth fails to perfectly fit in the nozzle. Therefore, a user notices the connection mistake of the pipes. Alternatively, the pipes may have different cross sections (e.g., round, rectangular or triangular cross sections).

[0029] Upon completion of the connection of the breath sampling bag 1, the spectrometric apparatus performs the following automatic control.

II. Apparatus for spectrometrically measuring isotopic gas

[0030] Fig. 7 is a block diagram illustrating the overall construction of the apparatus for spectrometrically measuring an isotopic gas.

[0031] The breath sampling bag is set to the apparatus so that one breath sampling chamber thereof containing the breath sampled after the drug administration (hereinafter referred to as "sample gas") and the other breath sampling chamber thereof containing the breath (hereinafter referred to as "base gas") , sampled before the drug administration are connected to the nozzles N_1 and N_2, respectively. The nozzle N_1 is connected to one port of a three-way valve V_1 through a transparent resin pipe (hereinafter referred to simply as "pipe") and the nozzle N_2 is connected to one port of a three-way valve V_2 through a pipe.

[0032] A reference gas (any gas having no absorption at a wavelength for measurement, e.g., nitrogen gas) is supplied from a gas cylinder to the apparatus. The reference gas flows through a flow path diverged into two paths. One path is connected through a flow meter M_1 to a reference cell 11c. The other path is connected through a flow meter M_2 to one port of a three-way valve V_3. The reference gas flows into the reference cell 11c, and discharged therefrom.

[0033] The other ports of the three-way valve V_3 are connected to another port of the three-way valve V_1 and to a first sample cell 11a for measuring a $^{12}CO_2$ absorbance. The other ports of the three-way valve V_2 are connected to the first sample cell 11a through a two-way valve V_4 and to the other port of the three-way valve V_1.

[0034] A gas injector 21 (volume: 60cc) for quantitatively injecting the sample gas or the base gas is interposed between the three-way valve V_3 and the first sample cell 11a. The gas injector 21 is a syringe-like device having a piston and a cylinder. The piston is driven by cooperation of a motor, a screw connected to the motor and a nut fixed to the piston (which will be described later).

[0035] As shown in Fig. 7, a cell chamber 11 has the first sample cell 11a having a smaller length for measuring therein a $^{12}CO_2$ absorbance, a second sample cell 11b having a greater length for measuring therein a $^{13}CO_2$ absorbance, and the reference cell 11c through which the reference gas is passed. The first sample cell 11a communicates with the second sample cell 11b. The sample gas or the base gas is introduced into the first sample cell 11a and then into the second cell 11b, and discharged therefrom. The reference gas is introduced into the reference cell 11c, and then discharged therefrom. Specifically, the first and second sample cells 11a and 11b have lengths of 13mm and 250mm, respectively, and the reference cell 11c has a length of 236mm.

[0036] A discharge pipe extending from the second sample cell 11b is provided with an O_2 sensor 18. Usable as the O_2 sensor 18 are commercially available oxygen sensors such as a solid electrolyte gas sensor (e.g., zirconia sensor) and an electrochemical gas sensor (e.g., galvanic cell sensor).

[0037] A reference character L denotes an infrared light source having two waveguides 23a and 23b for guiding infrared rays for irradiation. The generation of the infrared rays may be achieved in any way. For example, a ceramic heater (surface temperature: 450°C) and the like can be used. A rotary chopper 22 for periodically blocking the infrared rays is provided adjacent to the infrared light source L. Infrared rays emitted from the infrared light source L are transmitted to the first sample cell 11a and the reference cell 11c through a first light path, and to the second sample cell 11b through a second light path (see Fig. 8).

[0038] A reference character D denotes an infrared detector for detecting the infrared rays transmitted through the cells. The infrared detector D has a first wavelength filter 24a and a first detection element 25a disposed in the first light path, and a second wavelength filter 24b and a second detection element 25b disposed in the second light path.

[0039] The first wavelength filter 24a (band width: about 20nm) passes an infrared ray having a wavelength of about 4,280nm to be used for measurement of a $^{12}CO_2$ absorbance. The second wavelength filter 24b (band width: about 50nm) passes an infrared ray having a wavelength of about 4,412nm to be used for measurement of a $^{13}CO_2$ absorbance. Usable as the first and second detection elements 25a and 25b are any elements capable of detecting infrared rays. For example, a semiconductor infrared sensor such as of PbSe is used.

[0040] The first wavelength filter 24a and the first detection element 25a are housed in a package 26a filled with an inert gas such as Ar. Similarly, the second wavelength filter 24b and the second detection element 25b are housed in a package 26b filled with an inert gas.

[0041] The whole infrared detector D is maintained at a constant temperature (25°C) by means of a heater and a Peltier element. The inside temperatures of the packages 26a and 26b are kept at 0°C by means of a Peltier element.

[0042] The cell chamber 11 is formed of a stainless steel, and vertically and laterally sandwiched between metal plates (e.g., brass plates) 12. A heater 13 is provided on upper, lower and lateral sides of the cell chamber. The cell chamber 11 is sealed with insulators 14 such as of polystyrene foam with the heater 13 interposed therebetween. Though not shown, a temperature sensor (e.g., a platinum temperature sensor) for measuring the temperature of the cell chamber 11 is provided in the cell chamber 11.

[0043] The cell chamber 11 has two tiers. The first sample cell 11a and the reference cell 11c are disposed in one tier, and the second sample cell 11b is disposed in the other tier.

[0044] The first light path extends through the first sample cell 11a and the reference cell 11c which are disposed in series, and the second light path extends through the second sample cell b. Reference characters 15, 16 and 17 denote sapphire transmission windows through which the infrared rays are transmitted.

[0045] Fig. 9 is a block diagram illustrating a mechanism for adjusting the temperature of the cell chamber 11. The temperature adjustment mechanism is constituted by the temperature sensor 32 provided in the cell chamber 11, a temperature adjustment substrate 31 and the heater 13. The temperature of the temperature adjustment substrate 31 may be adjusted in any manner. For example, the temperature adjustment can be achieved by changing the duty ratio of a pulse current flowing through the heater 13 on the basis of a temperature measurement signal of the temperature sensor 32. The heater 13 is controlled on the basis of this temperature adjustment method so as to maintain the cell chamber 11 at a constant temperature (40°,C).

[0046] Figs. 10A and 10B are a plan view and a side view, respectively, of the gas injector 21 for quantitativel injecting a gaseous sample.

[0047] The gas injector 21 includes a cylinder 21b disposed on a base 21a, a piston 21c inserted in the cylinder 21c, and a movable nut 21d connected to the piston 21c, a feed screw 21e threadingly meshed with the nut 21d and a motor 21f for rotating the feed screw 21e which are disposed below the base 21a.

[0048] The motor 21f is driven for forward and backward rotation by a driving circuit not shown. As the feed screw 21e is rotated by the rotation of the motor 21f, the nut 21d moved forward or backward depending on the rotational direction of the feed screw 21e. The piston 21c advances toward a position indicated by a dashed line in Fig. 10A. Thus, the gas injector 21 can be flexibly controlled to introduce and extract the gaseous sample in/from the cylinder 21b.

IIIa. Measuring procedure 1

[0049] The measuring procedure includes reference gas measurement, base gas measurement, reference gas measurement, sample gas measurement and reference gas measurement, which are to be performed in this order. Alternatively, base gas measurement, reference gas measurement and base gas measurement, and sample gas measurement, reference gas measurement and sample gas measurement may be performed in this order. In the latter case, the base gas measurement and the sample gas measurement are each performed twice and, therefore, the operation efficiency is reduced. The former measuring procedure which is more efficient will hereinafter be described.

[0050] During the measurement, the reference gas constantly flows through the reference cell 11c, and the flow rate

thereof is always kept constant by the flow meter M_1.

IIIa-1. Reference measurement

[0051] As shown in Fig. 11, the clean reference gas is passed through a gas flow path and the cell chamber 11 of the spectrometric apparatus at a rate of 200ml/minute for about 15 seconds for cleaning the gas flow path and the cell chamber 11.

[0052] In turn, as shown in Fig. 12, the gas flow path is changed, and then the reference gas is passed therethrough for cleaning the gas flow path and the cell chamber 11. After a lapse of about 30 seconds, light intensity are measured by means of the detection elements 25a and 25b.

[0053] On the basis of the reference measurement, absorbances are calculated.

[0054] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by $^{12}R_1$ and $^{13}R_1$, respectively.

IIIa-2. Base gas measurement

[0055] The base gas is sucked into the gas injector 21 from the breath sampling bag with the reference gas prevented from flowing through the first and second sample cells 11a and 11b (see Fig. 13).

[0056] Thereafter, the base gas is mechanically pushed out at a constant rate (60ml/minute) by the gas injector 21 as shown in Fig. 14 and, at the same time, light intensity are measured by means of the detection elements 25a and 25b.

[0057] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by ^{12}B and ^{13}B, respectively.

IIIa-3. Reference measurement

[0058] The cleaning of the gas flow path and the cells and the light intensity measurement on the reference gas are performed again (see Figs. 11 and 12).

[0059] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by $^{12}R_2$ and $^{13}R_2$, respectively.

IIIa-4 . Sample gas measurement

[0060] The sample gas is sucked into the gas injector 21 from the breath sampling bag with the reference gas prevented from flowing through the first and second sample cells 11a and 11b (see Fig. 15).

[0061] Thereafter, the sample gas is mechanically pushed out at a constant rate (60ml/minute) by the gas injector 21 as shown in Fig. 16 and, at the same time, light intensity are measured by means of the detection elements 25a and 25b.

[0062] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by ^{12}S and ^{13}S, respectively.

IIIa-5. Reference measument

[0063] The cleaning of the gas flow path and the cells and the light intensity measurement on the reference gas are performed again (see Figs. 11 and 12).

[0064] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by $^{12}R_3$ and $^{13}R_3$, respectively.

IIIb. Measurement procedure 2

[0065] In the measurement procedure 1, the CO_2 concentrations of the base gas and the sample gas are not adjusted to the same level.

[0066] If the base gas and the sample gas are at the same CO_2 concentration level, the ranges of $^{12}CO_2$ and $^{13}CO_2$ calibration curves to be used for determination of the concentrations can be narrowed. By using limited ranges of the calibration curves, the measurement accuracy can be increased.

[0067] In accordance with the measurement procedure 2, the CO_2 concentrations of the base gas and the sample gas are adjusted to substantially the same level. First, the CO_2 concentrations of the base gas and the sample gas are measured in a preliminary measurement. If the CO_2 concentration of the base gas obtained in the preliminary measurement is higher than the CO_2 concentration of the sample gas obtained in the preliminary measurement, the

base gas is diluted to a CO_2 concentration level equivalent to that of the sample gas, and the measurement of the concentration is performed on the base gas and then on the sample gas in a main measurement.

[0068] If the CO_2 concentration of the base gas obtained in the preliminary measurement is lower than the CO_2 concentration of the sample gas obtained in the preliminary measurement, the CO_2 concentration of the base gas is measured in the main measurement. The sample gas is diluted to a CO_2 concentration level equivalent to that of the base gas, and then the CO_2 concentration thereof is measured.

[0069] The measurement procedure 2 includes preliminary base gas measurement, preliminary sample gas measurement, reference gas measurement, base gas measurement, reference gas measurement, sample gas measurement and reference gas measurement, which are performed in this order.

IIIb-1. Preliminary base gas measurement

[0070] The clean reference gas is passed through the gas flow path and the cell chamber 11 of the spectrometric apparatus for cleaning the gas flow path and the cell chamber 11 and, at the same time, a reference light intensity is measured.

[0071] In turn, the base gas is sucked into the gas injector 21 from the breath sampling bag, and then mechanically pushed out at a constant flow rate by means of the gas injector 21. At this time, the intensity of light transmitted through the base gas is measured by means of the detection element 25a to determine an absorbance, and the CO_2 concentration of the base gas is determined on the basis of the absorbance by using a calibration curve.

IIIb-2. Preliminary sample gas measurement

[0072] The clean reference gas is passed through the gas flow path and the cell chamber 11 of the spectrometric apparatus for cleaning the gas flow path and the cell chamber 11 and, at the same time, a reference light intensity is measured.

[0073] In turn, the sample gas is sucked into the gas injector 21 from the breath sampling bag, and then mechanically pushed out at a constant flow rate by means of the gas injector 21. At this time, the intensity of light transmitted through the sample gas is measured by means of the detection element 25a to determine an absorbance, and the CO_2 concentration of the sample gas is determined on the basis of the absorbance by using the calibration curve.

IIIb-3. Reference measurement

[0074] The gas flow path is changed, and then the reference gas is passed therethrough to clean the gas flow path and the cell chamber 11. After a lapse of about 30 seconds, light intensity. are measured by means of the detection elements 25a and 25b.

[0075] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by $^{12}R_1$ and $^{13}R_1$, respectively.

IIIb-4. Base gas measurement

[0076] The CO_2 concentration of the base gas obtained by the first detection element 25a in "IIIb-1. Preliminary base gas measurement" is compared with the CO_2 concentration of the sample gas obtained by the first detection, element 25a in "IIIb-2. Preliminary sample gas measurement". If the CO_2 concentration of the base gas is higher than the CO_2 concentration of the sample gas, the base gas is diluted with the reference gas in the gas injector 21 to a CO_2 concentration level equivalent to that of the sample gas, and then the light intensity measurement is performed on the base gas thus diluted.

[0077] Since the CO_2 concentrations of the two breath samples are adjusted to substantially the same level by dilution, the ranges of the $^{12}CO_2$ and $^{13}CO_2$ calibration curves to be used can be narrowed.

[0078] It should be noted that the measuring procedure 2 of this embodiment is characterized in that the CO_2 concentrations of the two breath samples are adjusted to substantially the same level, and does not necessarily require to employ a step of maintaining the CO_2 concentration at a constant level as described in JPB 4(1992)-124141. The use of limited ranges of calibration curves can be achieved simply by adjusting the CO_2 concentrations of the base gas and the sample gas to substantially the same level. Since the CO_2 concentrations of the base gas and the sample gas vary within a range of 1% to 5% in actual measurement, it is very troublesome to always maintain the CO_2 concentrations at a constant level.

[0079] If the CO_2 concentration of the base gas is lower than the CO_2 concentration of the sample gas, the base gas is not diluted, and the measurement is performed on the base gas.

[0080] The base gas is mechanically pushed out at a constant flow rate by the gas injector 21, and light intensity are

measured by means of the detection elements 25a and 25b.

[0081] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by ^{12}B and ^{13}B, respectively.

IIIb-5. Reference measurement

[0082] The cleaning of the gas flow path and the cells and the light intensity measurement on the reference gas are performed again.

[0083] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by $^{12}R_2$ and $^{13}R_2$, respectively.

IIIb-6. Sample gas measurement

[0084] If the base gas is diluted in "IIIb-4. Base gas measurement", the sample gas is sucked from the breath sampling bag, and then mechanically pushed out at a constant flow rate by the gas injector 21. At this time, light intensity are measured by the detection elements 25a and 25b.

[0085] If the base gas is not diluted in "IIIb-4. Base gas measurement", the sample gas is diluted with the reference gas to a CO_2 concentration level equivalent to that of the base gas in the gas injector 21, and then the intensity of light transmitted through the sample gas is measured by means of the detection elements 25a and 25b.

[0086] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by ^{12}S and ^{13}S, respectively.

IIIb-7. Reference measurement

[0087] The cleaning of the gas flow path and the cells and the light intensity measurement on the reference gas are performed again.

[0088] The light intensity thus obtained by the first and second detection elements 25a and 25b are represented by $^{12}R_3$ and $^{13}R_3$, respectively.

IV. Data processing

IV-1. Calculation of absorbances for base gas

[0089] Absorbances $^{12}Abs(B)$ and $^{13}Abs(B)$ of $^{12}CO_2$ and $^{13}CO_2$ in the base gas are calculated on the basis of the transmitted light intensity $^{12}R_1$, $^{13}R_1$, $^{12}R_2$ and $^{13}R_2$ for the reference gas and the transmitted light intensity ^{12}B and ^{13}B for the base gas obtained in the measuring procedure 1 or in the measuring procedure 2.

[0090] The absorbance $^{12}Abs(B)$ of $^{12}CO_2$ is calculated from the following equation:

$$^{12}Abs(B)=-\log[2\cdot{}^{12}B/(^{12}R_1+{}^{12}R_2)]$$

[0091] The absorbance $^{13}Abs(B)$ of $^{13}CO_2$ is calculated from the following equation:

$$^{13}Abs(B)=-\log[2\cdot{}^{13}B/(^{13}R_1+{}^{13}R_2)]$$

[0092] Since the calculation of the absorbances is based on the light intensity obtained in the base gas measurement and the averages $(^{12}R_1+{}^{12}R_2)/2$ and $(^{13}R_1+{}^{13}R_2)/2$ of the light intensity obtained in the reference measurements performed before and after the base gas measurement, the influence of a drift (a time-related influence on the measurement) can be eliminated. Therefore, when the apparatus is ,turned on, there is no need for waiting until the apparatus reaches a thermal equilibrium (it usually takes several hours).

[0093] Where the measuring procedure of the base gas measurement, the reference gas measurement and the base gas measurement, and the sample gas measurement, the reference gas measurement and the sample gas measurement as describe at the beginning of "IIIa" is employed, the absorbance $^{12}Abs(B)$ of $^{12}CO_2$ in the base gas is calculated from the following equation:

$$^{12}Abs(B)=-\log[(^{12}B_1+{}^{12}B_2)/2\cdot{}^{12}R]$$

and the absorbance ^{13}Abs (B) of $^{13}CO_2$ is calculated from the following equation:

$$^{13}Abs(B)=-\log[(^{13}B_1+^{13}B_2)/2\cdot^{13}R]$$

wherein ^{12}R and ^{13}R are the transmitted light intensity for the reference gas, $^{12}B_1$ and $^{13}B_1$ are the transmitted light intensity for the base gas obtained before the reference gas measurement, and $^{12}B_2$ and $^{13}B_2$ are the transmitted light intensity for the base gas obtained after the reference gas measurement.

IV-2. Calculation of absorbances for sample gas

[0094] Absorbances ^{12}Abs(S) and ^{13}Abs(S) of $^{12}CO_2$ and $^{13}CO_2$ in the sample gas are calculated on the basis of the transmitted light intensity $^{12}R_2$, $^{13}R_2$, $^{12}R_3$ and $^{13}R_3$ for the reference gas and the transmitted light intensity ^{12}S and ^{13}S for the sample gas obtained in the measuring procedure 1 or in the measuring procedure 2.

[0095] The absorbance ^{12}Abs(S) of $^{12}CO_2$ is calculated from the following equation:

$$^{12}Abs(S)=-\log[2\cdot^{12}S/(^{12}R_2+^{12}R_3)]$$

[0096] The absorbance ^{13}Abs(S) of $^{13}CO_2$ is calculated from the following equation:

$$^{13}Abs(S)=-\log[2\cdot^{13}S/(^{13}R_2+^{13}R_3)]$$

[0097] Since the calculation of the absorbances is based on the light intensity obtained in the sample gas measurement and the averages of the light intensity obtained in the reference measurements performed before and after the sample gas measurement, the influence of a drift can be eliminated.

[0098] Where the measuring procedure of the base gas measurement, the reference gas measurement and the base gas measurement, and the sample gas measurement, the reference gas measurement and the sample gas measurement as describe at the beginning of "IIIa" is employed, the absorbance ^{12}Abs(S) of $^{12}CO_2$ in the sample gas is calculated from the following equation:

$$^{12}Abs(S)=-\log[(^{12}S_1+^{12}S_2)/2\cdot^{12}R]$$

and the absorbance ^{13}Abs(S) of $^{13}CO_2$ is calculated from the following equation:

$$^{13}Abs(S)=-\log[(^{13}S_1+^{13}S_2)/2\cdot^{13}R]$$

wherein ^{12}R and ^{13}R are the transmitted light intensity for the reference gas, $^{12}S_1$ and $^{13}S_1$ are the transmitted light intensity for the sample gas obtained before the reference gas measurement, and $^{12}S_2$ and $^{13}S_2$ are the transmitted light intensity for the sample gas obtained after the reference gas measurement.

IV-3. Calculation of concentrations

[0099] The $^{12}CO_2$ concentration and the $^{13}CO_2$ concentration are calculated by using calibration curves.

[0100] The calibration curves for $^{12}CO_2$ and $^{13}CO_2$ are prepared on the basis of measurement performed by using gaseous samples of known $^{12}CO_2$ concentrations and gaseous samples of known $^{13}CO_2$ concentrations, respectively.

[0101] For preparation of the calibration curve for $^{12}CO_2$, the $^{12}CO_2$ absorbances for different $^{12}CO_2$ concentrations within a range of about 0% to about 6% are measured. The $^{12}CO_2$ concentrations and the $^{12}CO_2$ absorbances are plotted as abscissa and ordinate, respectively, and the curve is determined by the method of least squares, An approximate quadratic curve, which includes relatively small errors, is employed as the calibration curve in this embodiment.

[0102] For preparation of the calibration curve for $^{13}CO_2$, the $^{13}CO_2$ absorbances for different $^{13}CO_2$ concentrations within a range of about 0.00% to about 0.07% are measured. The $^{13}CO_2$ concentrations and the $^{13}CO_2$ absorbances are plotted as abscissa and ordinate, respectively, and the curve is determined by the method of least squares. An approximate quadratic curve, which includes relatively small errors, is employed as the calibration curve in this em-

bodiment.

[0103] Strictly speaking, the $^{13}CO_2$ absorbance determined by individually measuring gases respectively containing $^{12}CO_2$ and $^{13}CO_2$ may be different from the $^{13}CO_2$ absorbance determined by measuring a gas containing both $^{12}CO_2$ and $^{13}CO_2$. This is because the wavelength filters each have a bandwidth and the $^{12}CO_2$ absorption spectrum partially overlaps $^{13}CO_2$ absorption spectrum. Since gases containing both $^{12}CO_2$ and $^{13}CO_2$ are to be measured in this measurement method, the overlap of these spectra should be corrected for preparation of the calibration curves. The calibration curves to be employed in this measurement are subjected to the correction for the overlap of the absorption spectra.

[0104] For preparation of the calibration curve for the $^{12}CO_2$ concentration, the $^{12}CO_2$ absorbances for 20 different $^{12}CO_2$ concentions within a range of about 0% to about 6% are measured. The $^{12}CO_2$ concentrations and the $^{12}CO_2$ absorbances are plotted as abscissa and ordinate, respectively, as shown in Fig. 17A.

[0105] The curve, which passes through the respective data points, is determined by the method of least squares. An approximate quadratic curve includes the least error. Therefore, the approximate quadratic curve is employed as the calibration curve for $^{12}CO_2$ in this embodiment.

[0106] In turn, five data points are selected which are located around the $^{12}CO_2$ concentration of the base gas previously determined on the basis of the calibration curve for $^{12}CO_2$. The five data points fall within a concentration range of 1.5%, which accounts for 25% of the entire concentration range (6%) of the calibration curve shown in Fig. 17A. Then, the data within the limited concentration range are used for the preparation of a new calibration curve (see Fig. 17B). It is confirmed that the preparation of the calibration curve within the limited data range improves the conformity of the data to the approximate curve, thereby remarkably reducing errors associated with the preparation of the calibration curve. The $^{12}CO_2$ concentration of the base gas is determined on the basis of the absorbance $^{12}Abs(B)$ of the base gas by using the new calibration curve for $^{12}CO_2$.

[0107] The $^{12}CO_2$ concentration of the sample gas is determined in the same manner.

[0108] For preparation of the calibration curve for the $^{13}CO_2$ concentration, the $^{13}CO_2$ absorbances for 20 different $^{13}CO_2$ concentrations within a range of about 0.00% to about 0.07% are measured. The $^{13}CO_2$ concentrations and the $^{13}CO_2$ absorbances are plotted as abscissa and ordinate, respectively, as shown in Fig. 18A.

[0109] The curve, which passes through the respective data points, is determined by the method of least squares. An approximate quadratic curve includes the least error. Therefore, the approximate quadratic curve is employed as the calibration curve for $^{13}CO_2$ in this embodiment.

[0110] In turn, five data points are selected which are located around the $^{13}CO_2$ concentration of the base gas previously determined on the basis of the calibration curve for $^{13}CO_2$. The five data points fall within a concentration range of 0.015%, which accounts for about 1/4 of the entire concentration range (0.07%) of the calibration curve shown in Fig. 18A. Then, the data within the limited concentration range are used for the preparation of a new calibration curve (see Fig. 18B). It is confirmed that the preparation of the calibration curve within the limited data range improves the conformity of the data to the approximate curve, thereby remarkably reducing errors associated with the preparation of the calibration curve. The $^{13}CO_2$ concentration of the base gas is determined on the basis of the absorbance $^{13}Abs(B)$ of the base gas by using the new calibration curve for $^{13}CO_2$.

[0111] The $^{13}CO_2$ concentration of the sample gas is determined in the same manner.

[0112] The $^{12}CO_2$ concentration and $^{13}CO_2$ concentration of the base gas are represented by $^{12}Conc(B)$ and $^{13}Conc(B)$, respectively. The $^{12}CO_2$ concentration and $^{13}CO_2$ concentration of the sample gas are represented by $^{12}Conc(S)$ and $^{13}Conc(S)$, respectively.

IV-A. Calculation of concentration ratios

[0113] The concentration ratio of $^{13}CO_2$ to $^{12}CO_2$ is determined. The concentration ratios in the base gas and in the sample gas are expressed as $^{13}Conc(B)/^{12}Conc(B)$ and $^{13}Conc(S)/^{12}Conc(S)$, respectively.

[0114] Alternatively, the concentration ratios in the base gas and in the sample gas may be defined as $^{13}Conc(B)/^{12}Conc(B)+^{13}Conc(B)$ and $^{13}Conc(S)/^{12}Conc(S)+^{13}Conc(S)$, respectively. Since the $^{12}CO_2$ concentration is much higher than the $^{13}CO_2$ concentration, the concentration ratios expressed in the former way and in the latter way are substantially the same.

IV-5a. Correction of concentration ratios

[0115] As described in "BACKGROUND ART", the concentration ratios obtained in the aforesaid manner deviate from actual concentrations, depending on the $^{12}CO_2$ concentration.

[0116] Although the cause of the deviation has not been elucidated yet, une deviation supposedly results from changes in the spectroscopic characteristics such as reflectance, refractive index and stray light in dependence on the $^{12}CO_2$ concentration and from the error characteristics of the least square method employed for preparation of the calibration

curves.

[0117] If the concentration ratio is determined without correcting the deviation, a critical error may result. Therefore, absorbances ^{12}Abs and ^{13}Abs of $^{12}CO_2$ and $^{13}CO_2$ in gaseous samples having the same concentration ratio but different $^{12}CO_2$ concentrations are measured, and the $^{13}CO_2$ and $^{12}CO_2$ concentrations and $^{13}CO_2$ concentration ratios of the gaseous samples are determined by using the calibration curves. Then, the $^{12}CO_2$ concentrations ^{12}Conc and the concentration ratios ^{13}Conc/^{12}Conc are plotted as abscissa and ordinate, respectively.

[0118] The result is shown in Fig. 1.

[0119] The concentration ratios plotted as ordinate in the graph of Fig.1 are not normalized. The concentration ratios may be normalized for easy processing of data. Fig. 19 illustrates a graph obtained by way of standardization of the concentration ratios in which a concentration ratio in a gaseous sample of the lowest CO_2 concentration is regarded as "1". (The concentration ratios thus normalized are hereinafter referred to as "normalized concentration ratios".)

[0120] To obtain an approximate curve accommodating these plotted data, the method of least squares is employed for approximation of the data. It is experientially known that a function of the fourth degree expressed by the following equation (1) provides the most accurate approximate curve.

$$F(x) = ax^4 + bx^3 + cx^2 + dx + e \quad (1)$$

wherein F is a normalized concentration ratio, a to d are coefficients, e is a constant, and x is a $^{12}CO_2$ concentration. Therefore, the fourth-order function (1) is used as a correction equation. Alternatively, a spline function may be used.

[0121] Standardized $^{13}CO_2/^{12}CO_2$ concentration ratios are calculated from the correction equation (1) on the basis of the $^{12}CO_2$ concentrations ^{12}Conc(B) and ^{12}Conc(S) in the breath samples of the patient. Then, the concentration ratios ^{13}Conc(B)/^{12}Conc(B) and ^{13}Conc(S)/^{12}Conc(S) of the base gas and the sample gas obtained in the measurement are respectively divided by the normalized concentration ratios calculated from the correction equation (1). Thus, corrected concentration ratios are obtained as follows:

$$\text{Corrected concentration ratio} = {}^{13}\text{Conc(B)}/[{}^{12}\text{Conc(B)}\cdot F({}^{12}\text{Conc(B)})]$$

$$\text{Corrected concentration ratio} = {}^{13}\text{Conc(S)}/[{}^{12}\text{Conc(S)}\cdot F({}^{12}\text{Conc(S)})]$$

IV-5b. Correction of concentration ratios

[0122] The $^{13}CO_2$ concentration ratios of the base gas and the sample gas are subjected to a correction for oxygen concentration according to the present invention.

[0123] The $^{13}CO_2$ concentration ratios are corrected by using a graph (Fig. 2) in which measurements of the $^{13}CO_2$ concentration ratio are plotted with respect to the oxygen contents of gaseous samples.

[0124] More specifically, normalized $^{13}CO_2$ concentration ratios are obtained from the graph shown in Fig. 2 on the basis of the concentrations of oxygen in the breath samples which are measured by means of the O_2 sensor. Then, the $^{13}CO_2$ concentration ratios of the base gas and the sample gas are respectively divided by the normalized $^{13}CO_2$ concentration ratios. Thus, the $^{13}CO_2$ concentration ratios corrected depending on the oxygen concentrations can be obtained.

IV-6. Determination of change in ^{13}C

[0125] A difference in ^{13}C between the sample gas and the base gas is calculated from the following equation: $\Delta^{13}C$ = [Concentration ratio of sample gas - Concentration ratio of base gas] x 10^3 / [Concentration ratio of base gas] (Unit: per mil)

V. Modification

[0126] The present invention is not limited to the embodiment described above. In the above-mentioned embodiment, the $^{12}CO_2$ and $^{13}CO_2$ concentrations of the base gas and the sample gas are determined, then the concentration ratios thereof are calculated, and the concentration ratios are subjected to the oxygen concentration correction. Alternatively,

the concentration ratios may be determined after the $^{12}CO_2$ and $^{13}CO_2$ concentrations of the base gas and the sample gas are determined and the $^{12}CO_2$ and $^{13}CO_2$ concentrations are corrected by way of the oxygen concentration correction.

VI. Experiments

VI-1.

[0127] The absorbances of gaseous samples respectively, containing $^{12}CO_2$ in concentrations ^{12}Conc of 1%, 2%, 3%, 4%, 5% and 6% with a concentration ratio ^{13}Conc/^{12}Conc of 1.077% were measured in accordance with the method for spectrometrically measuring an isotopic gas. The $^{12}CO_2$ concentrations ^{12}Conc and $^{13}CO_2$ concentrations ^{13}Conc of the gaseous samples were determined on the basis of the measured absorbances by using the calibration curves. The $^{12}CO_2$ concentrations ^{12}Conc and the concentration ratios ^{13}Conc/^{12}Conc were plotted as abscissa and ordinate, respectively, as shown in Fig. 20.

[0128] The maximum and minimum values of the concentration ratios ^{13}Conc/^{12}Conc were 1.083% and 1.076%, respectively, and the difference therebetween was 0.007%.

[0129] In turn, the concentration ratios ^{13}conc/^{12}conc were corrected by using the correction equation (1), thus providing a less undulant curve as shown in Fig. 21. In Fig. 21, the maximum and minimum values of the concentration ratios ^{13}Conc/^{12}Conc were 1.078% and 1.076%, respectively, and the difference therebetween was 0.0015%.

[0130] Therefore, the correction with the correction equation (1) remarkably reduced the variation in the concentration ratio ^{13}Conc/^{12}Conc.

VT-2.

[0131] The absorbances of gaseous samples respectively containing $^{12}CO_2$ in concentrations ^{12}Conc of 1%, 2%, 3%, 4%, 5% and 6% with a concentration ratio ^{13}Conc/^{12}Conc of 1.065% were measured in accordance with the method for spectrometrically measuring an isotopic gas. The ^{12}Conc and the ^{13}Conc were determined on the basis of the measured absorbances by using the calibration curves shown in Figs. 17A and 18A. The $^{12}CO_2$ concentrations ^{12}Conc and the concentration ratios ^{13}Conc/^{12}Conc were plotted as abscissa and ordinate, respectively, as shown in Fig. 22.

[0132] The maximum and minimum values of the concentration ratios ^{13}Conc/^{12}Conc were 1.077% and 1.057%, respectively, and the difference therebetween was 0.02%.

[0133] In turn, concentration ratios ^{13}Conc/^{12}Conc were determined by using the calibration curves shown in Figs. 17A and 18A and then using the limited-range calibration curves shown in Figs. 17B and 18B, thus providing a less undulant curve as shown in Fig. 23. In Fig. 23, the maximum and minimum values of the concentration ratios ^{13}Conc/^{12}Conc were 1.066% and 1.064%, respectively, and the difference therebetween was 0.002%.

[0134] Therefore, the method of the present invention, in which the calibration curves were produced again, remarkably reduced the variation in the concentration ratio ^{13}Conc/^{12}Conc.

VI-3.

[0135] The absorbances of gaseous samples having different known $^{13}CO_2$ concentration ratios and containing various concentration of oxygen (up to 90%) were measured, and then the $^{13}CO_2$ concentration ratios were determined on the basis of the measured absorbances by using the calibration curves. Further, the $^{13}CO_2$ concentration ratios thus determined were corrected by using a correction line as shown in Fig. 2.

[0136] The actual $^{13}CO_2$ concentration ratios and the $^{13}CO_2$ concentration ratios thus corrected were normalized, and plotted as abscissa and ordinate; respectively, as shown in Fig. 24.

[0137] In Fig. 24, the relationship between the actual $^{13}CO_2$ concentration ratio and the measured $^{13}CO_2$ concentration ratio is about 1:1 (or the scope of the fitting curve in Fig. 24 is about 1). In comparison with the prior art shown in Fig. 4, in which the relationship between the actual $^{13}CO_2$ concentration ratio and the measured $^{13}CO_2$ concentration ratio is about 1:0.3 (or the scope of the fitting curve is about 0.3), the measurement accuracy was drastically improved by performing the correction.

[0138] Thus, the correction using the correction line remarkably improved the accuracy of the measurement of the $^{13}CO_2$ concentration ratio.

VI-4.

[0139] The $^{12}CO_2$ concentration of the same sample gas containing carbon dioxide was measured a plurality of times by means of the apparatus for spectrometrically measuring an isotopic gas.

[0140] After one hour warming-up of apparatus, a measuring procedure consisting of the reference gas measurement, the sample gas measurement, the reference gas measurement, the sample gas measurement and the reference gas measurement were performed ten times on the same sample gas. The $^{12}CO_2$ concentration was determined in each cycle of the measuring procedure in accordance with the method A of the present invention in which the absorbance of $^{12}CO_2$ in the sample gas was determined on the basis of an average of values obtained in the reference gas measurements performed before and after the sample gas measurement, and in accordance with the prior art method B in which the absorbance of $^{12}CO_2$ in the sample gas was determined on the basis of a value obtained in the reference measurement only before the sample gas measurement.

[0141] The results of the calculation of the concentrations in accordance with the method A are shown in Table 1. In Table 1, the concentrations obtained in the second and subsequent measurements were normalized by regarding a concentration obtained in the first measurement as "1". The standard deviation of the concentration data calculated in accordance with the method A was 0.0009.

Table 1

1	2	3	4	5
1	1.0011	0.9996	0.9998	1.0011
6	7	8	9	10
0.9982	1	1.0014	1.0005	1.0006

[0142] The results of the calculation of the concentrations in accordance with the method B are shown in Table 2. In Table 2, the concentrations obtained in the second and subsequent measurements were normalized by regarding a concentration obtained in the first measurement as "1". The standard deviation of the concentration data calculated in accordance with the method B was 0.0013.

Table 2

1	2	3.	4	5
1	1.0024	1.0001	0.9996	1.0018
6	7	8	9	10
0.9986	1	1.0022	1.0014	1.0015

[0143] As can be understood from the foregoing, the method of the present invention, in which the absorbances are determined on the basis of the light intensity measured on the sample gas and an average of the light intensity measured on the reference gas, provides concentration data with little variation.

Claims

1. An apparatus for spectrometrically measuring an isotopic gas, which is adapted to determine concentrations of a plurality of component gases in a gaseous test sample by introducing the gaseous test sample into a cell, then measuring intensity of light transmitted through the gaseous test sample at wavelengths suitable for the respective component gases, and processing data of the light intensity, **characterized by** gas injection means for sucking therein the gaseous test sample and then injecting the gaseous test sample into the cell by mechanically pushing out the gaseous test sample at a constant rate.

2. An apparatus as set forth in claim 1, further **characterized by** temperature maintaining means for maintaining the cell receiving the gaseous test sample introduced therein at a constant temperature.

FIG. 1
(PRIOR ART)

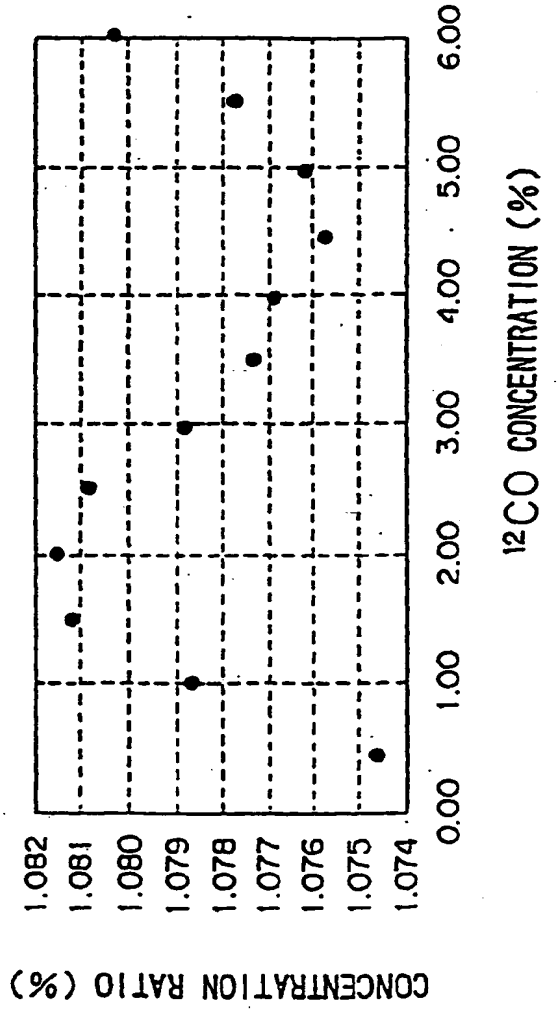


FIG. 2
(PRIOR ART)

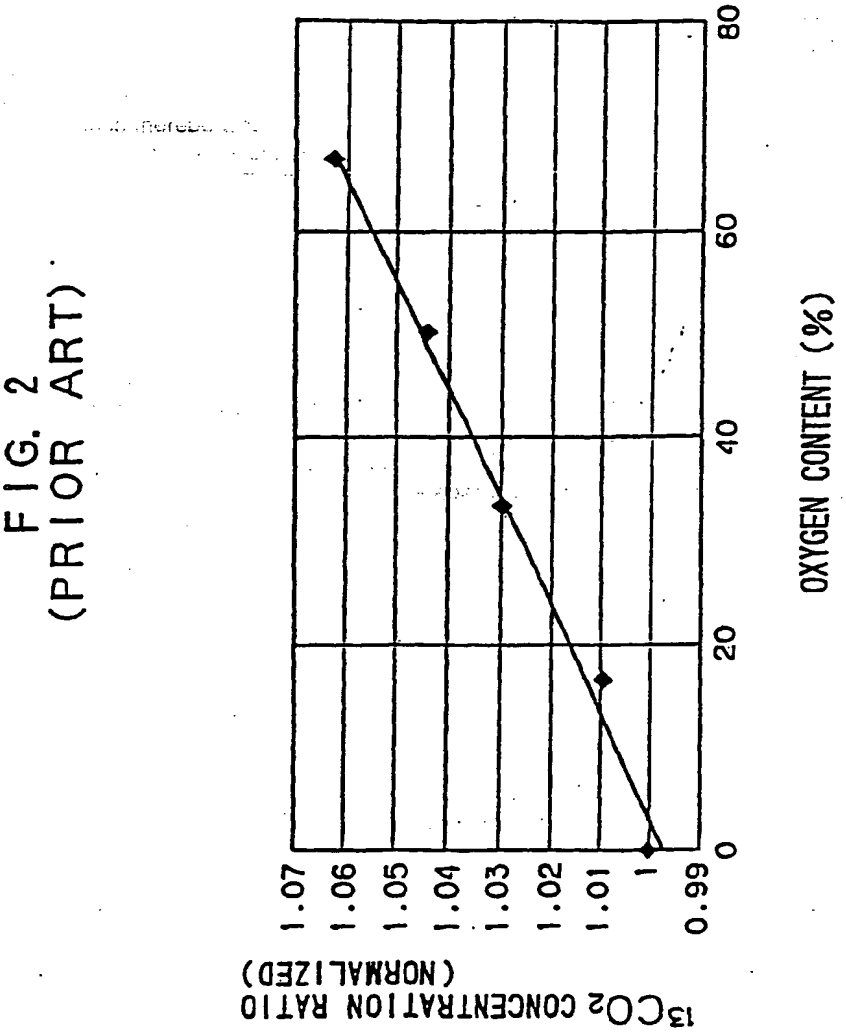


FIG. 3
(PRIOR ART)

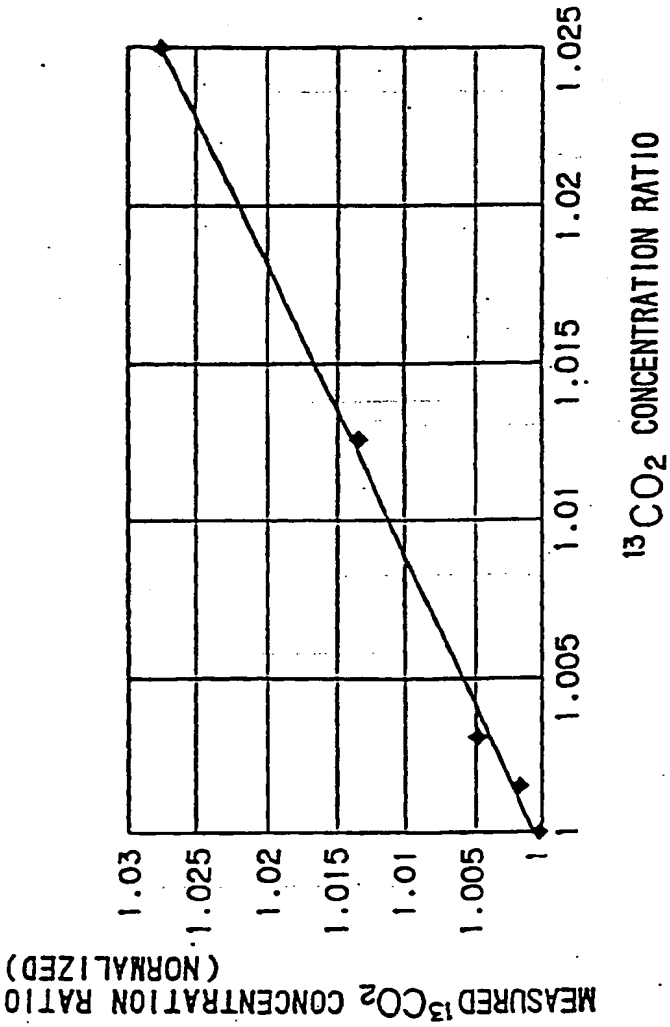


FIG. 4
(PRIOR ART)

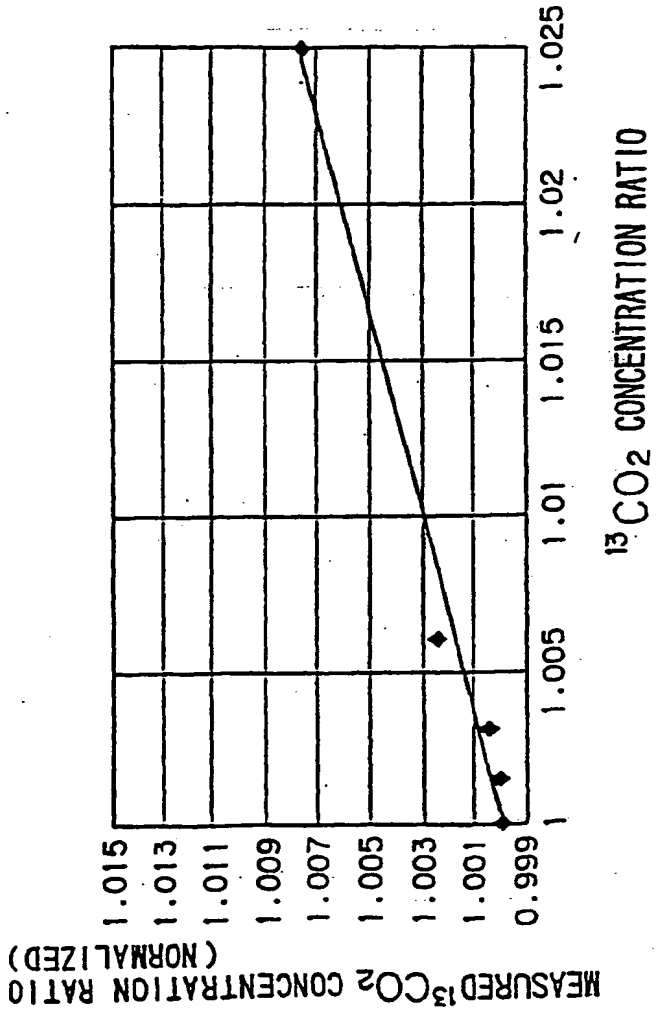


FIG. 5

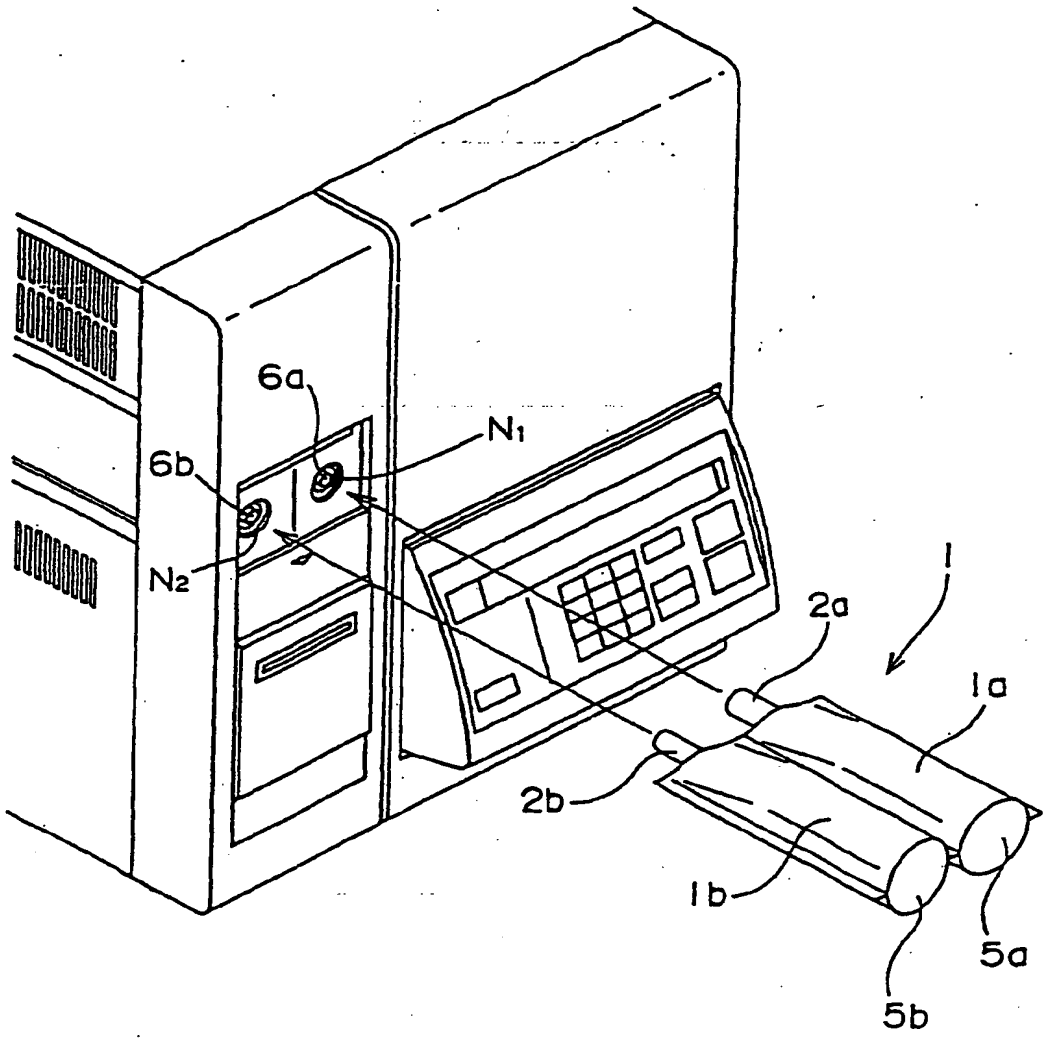


FIG. 6

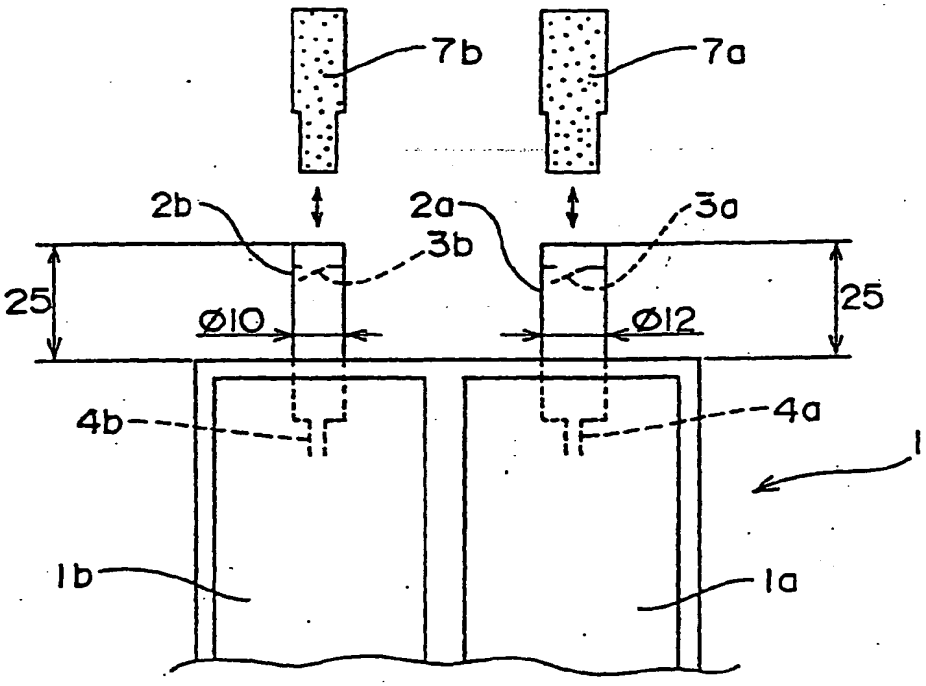
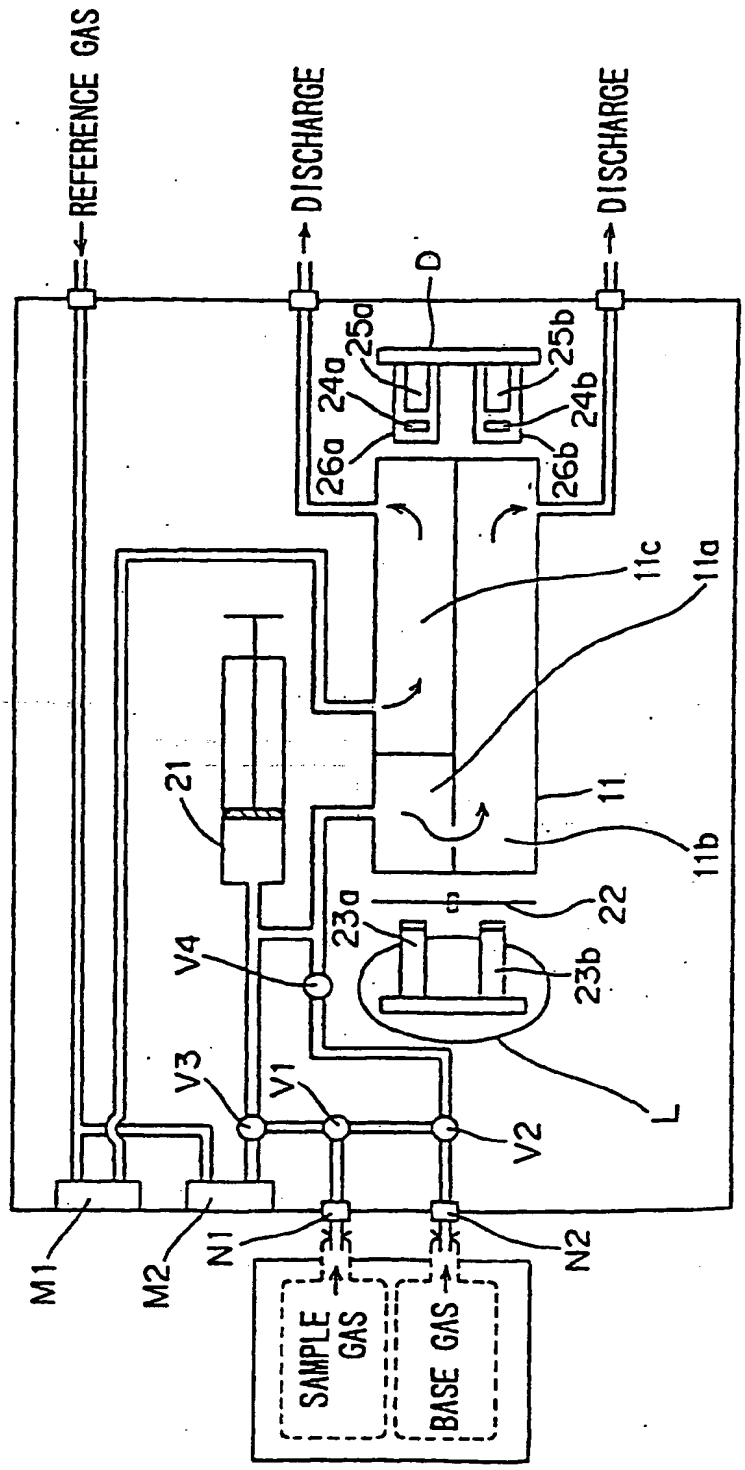


FIG. 7


REFERENCE GAS
DISCHARGE
DISCHARGE
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24b
26a
26b
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11
11b
21
22
23a
23b
V4
V3
V1
V2
L
M1
M2
N1
N2
SAMPLE GAS
BASE GAS

FIG. 8

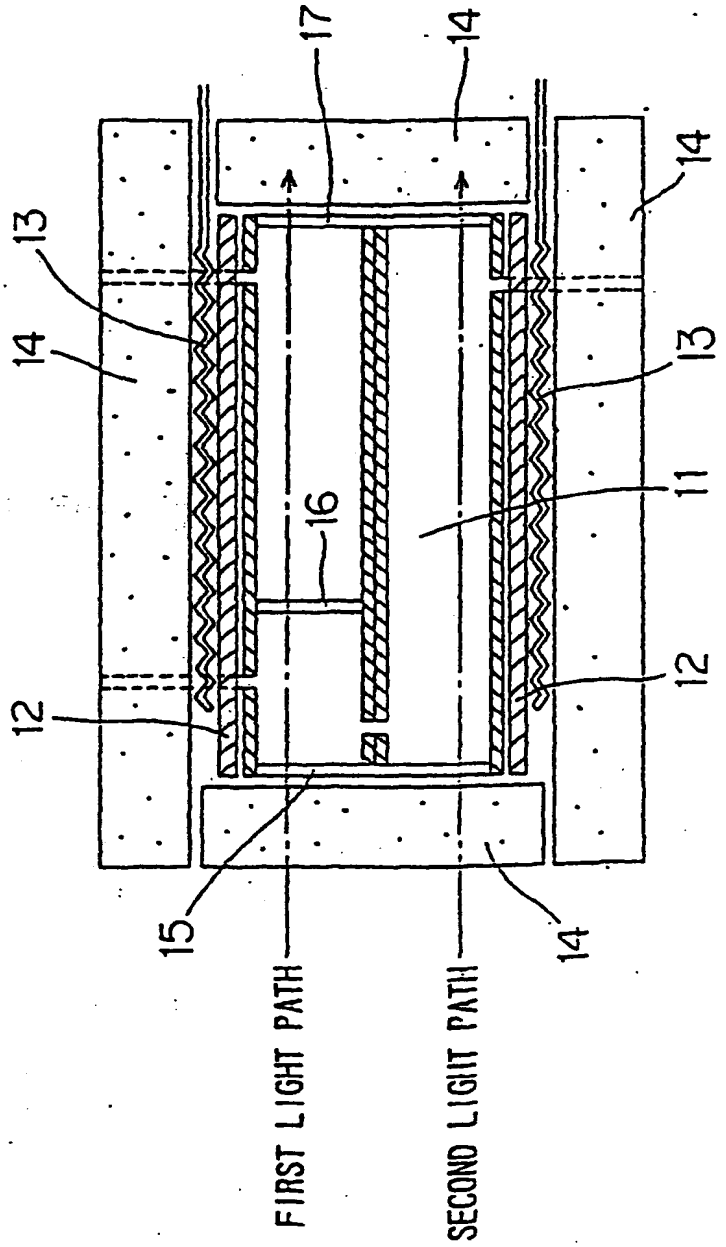

17
14
14
13
14
13
11
16
12
12
15
14
FIRST LIGHT PATH
SECOND LIGHT PATH

FIG. 9

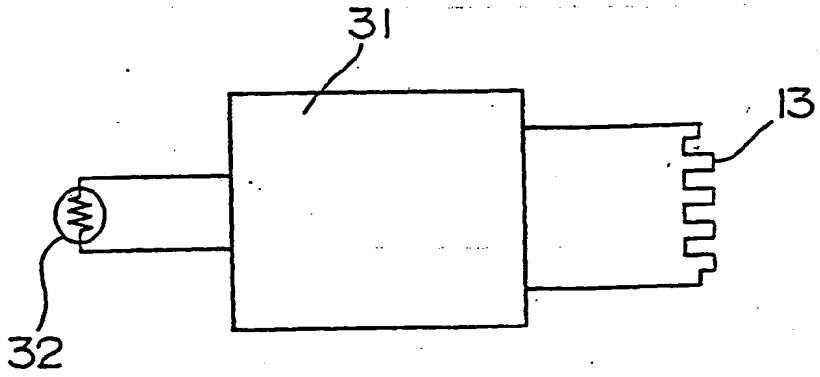


FIG. 10A

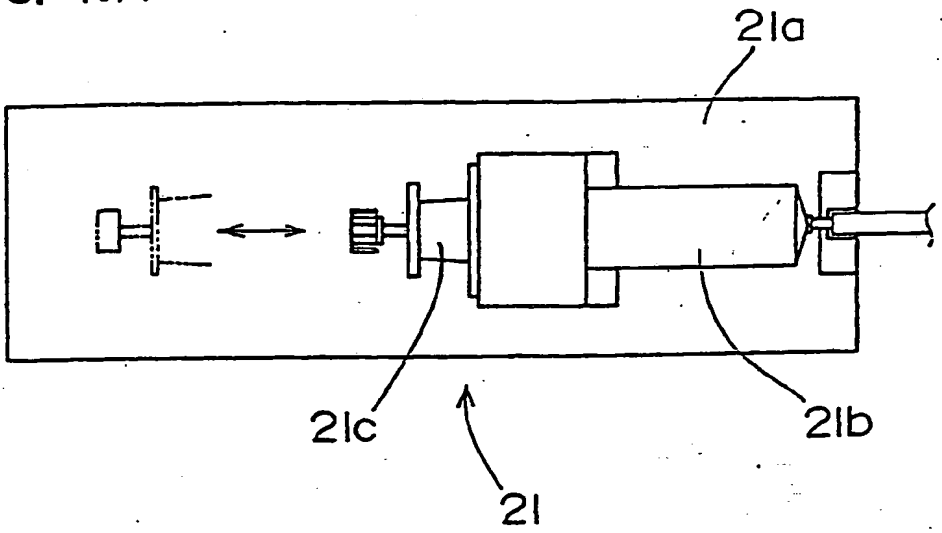


FIG. 10B

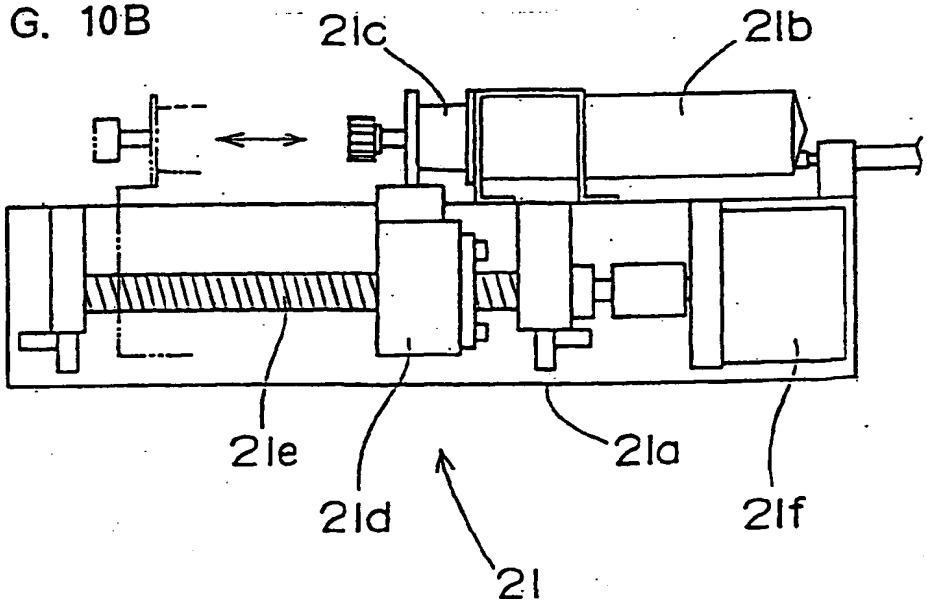


FIG. 11

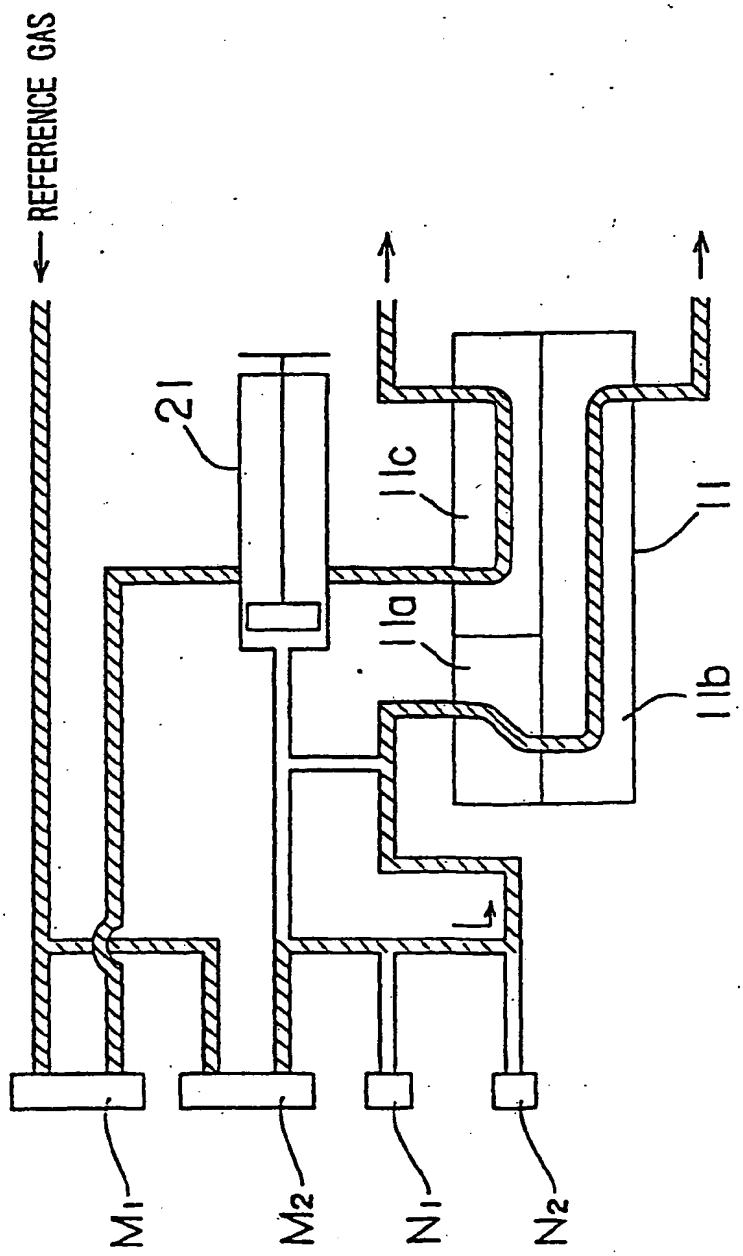


FIG. 12

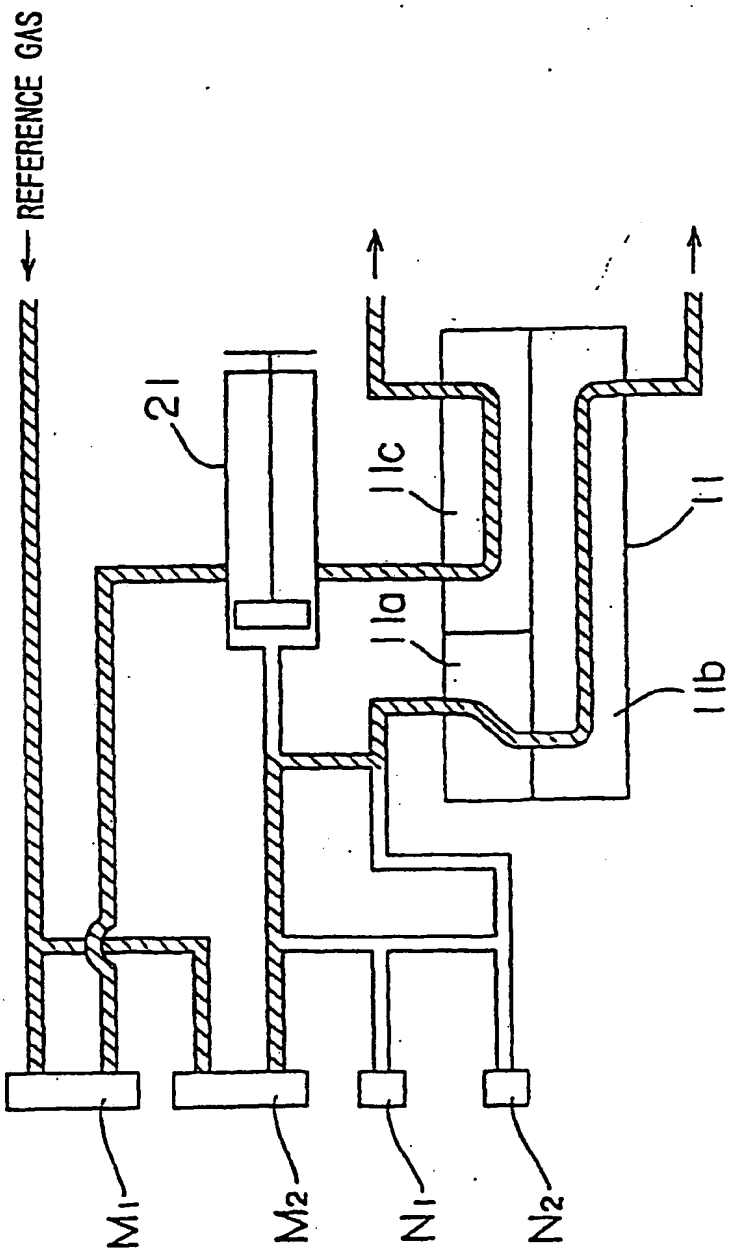


FIG. 13

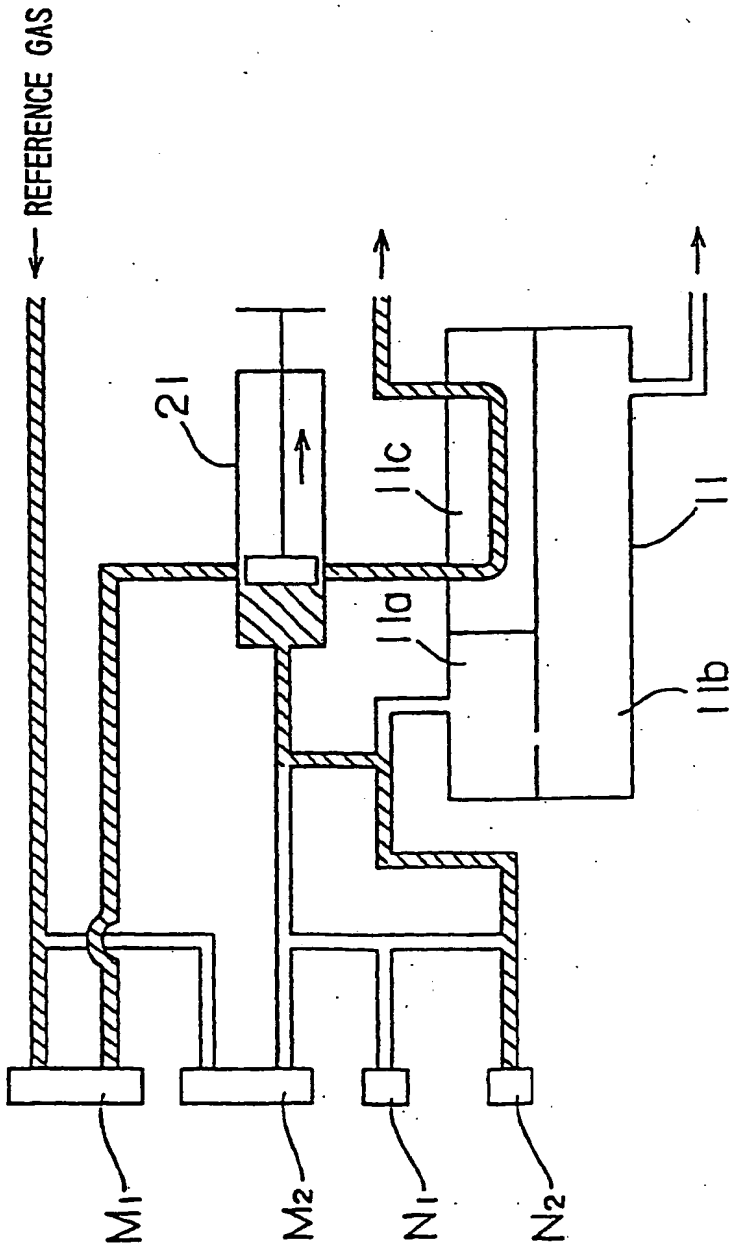


FIG. 14

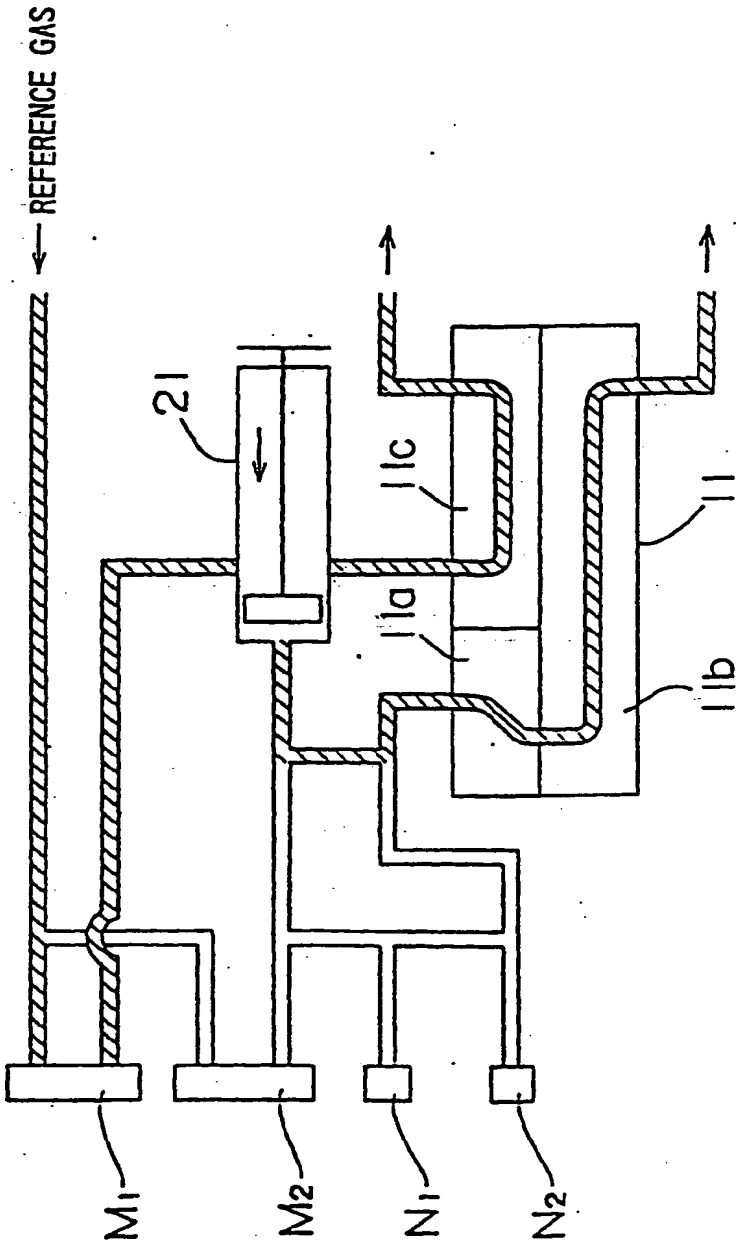


FIG. 15

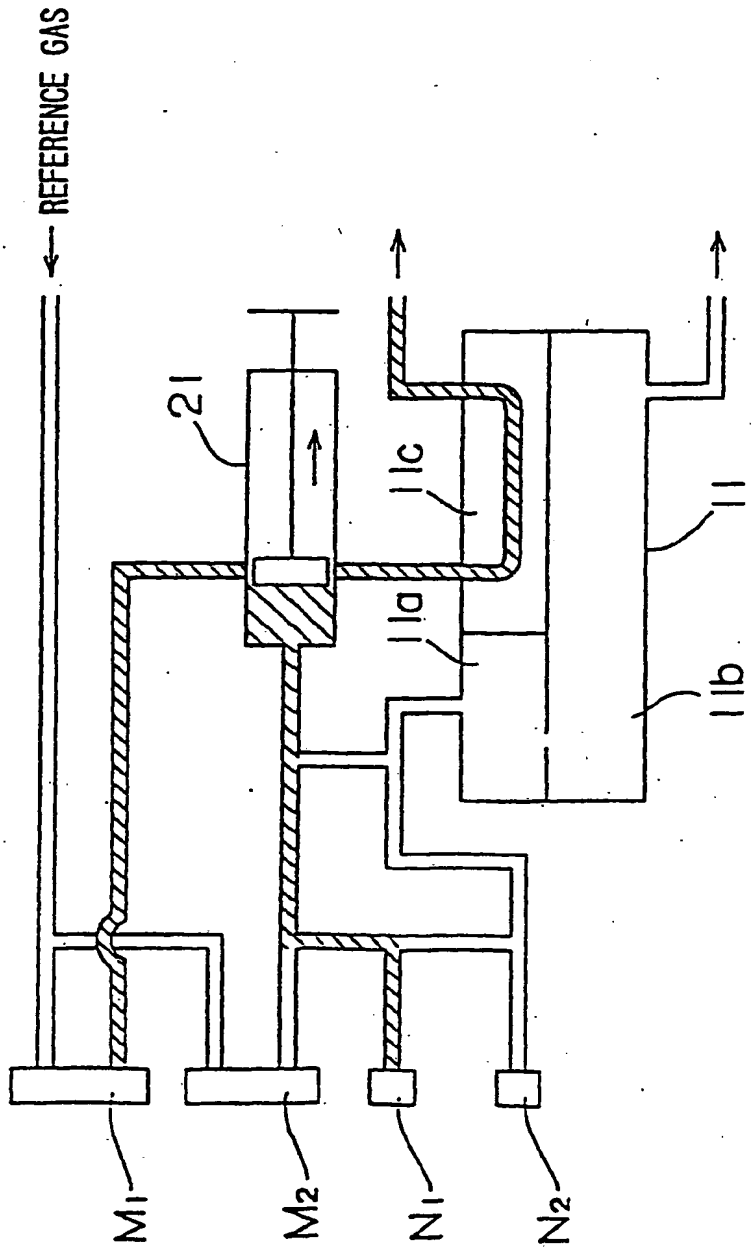


FIG. 16

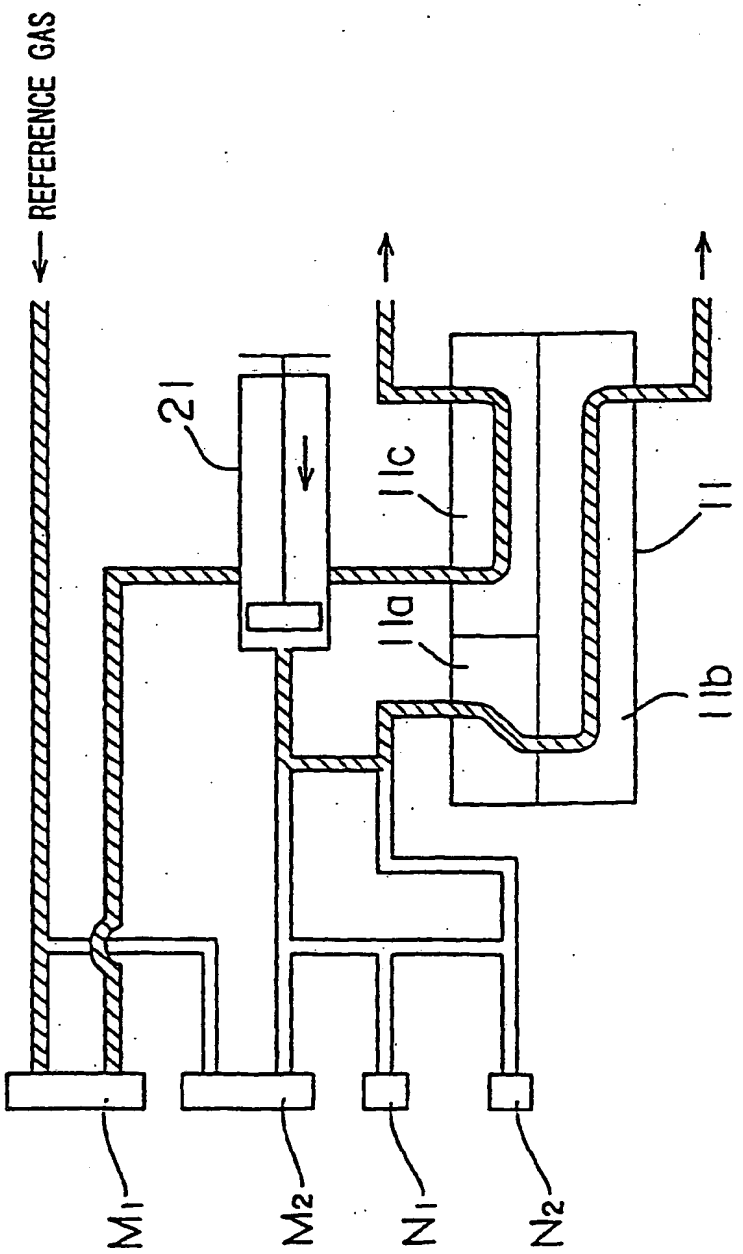


FIG. 17A

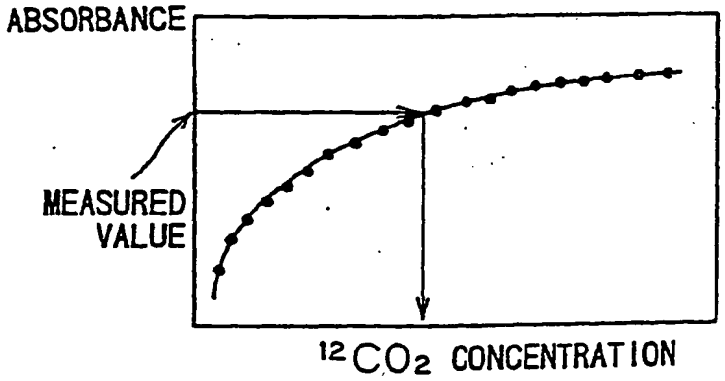


FIG. 17B

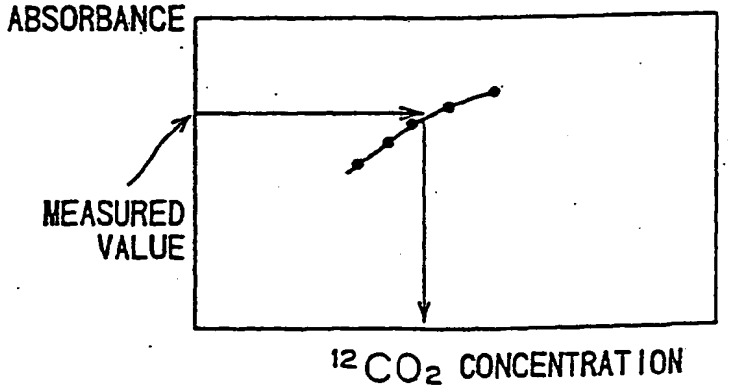


FIG. 18A

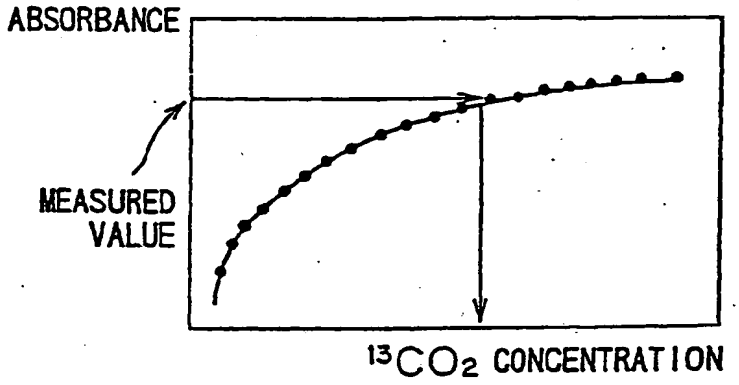


FIG. 18B

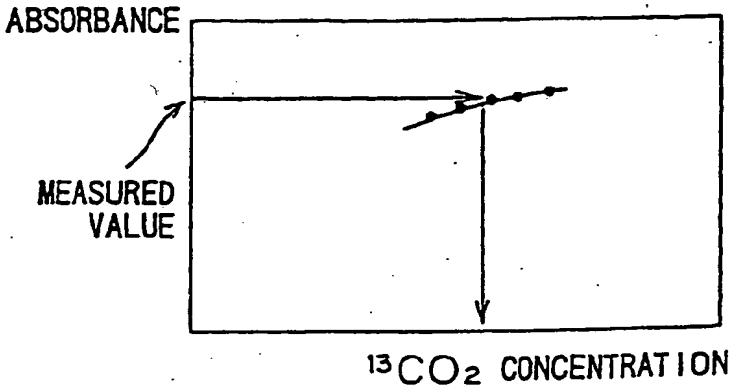


FIG. 19

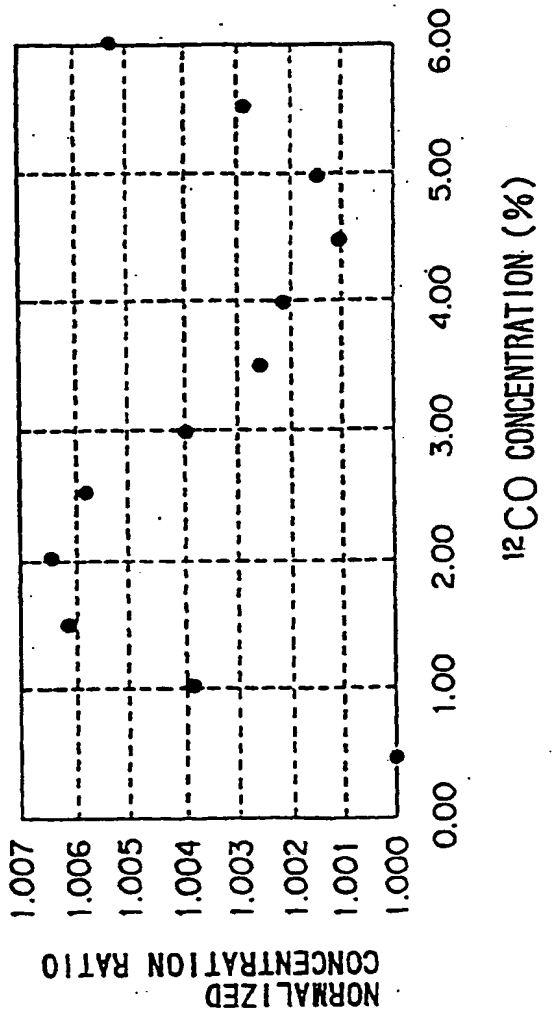

NORMALIZED CONCENTRATION RATIO
1.007
1.006
1.005
1.004
1.003
1.002
1.001
1.000
0.00
1.00
2.00
3.00
4.00
5.00
6.00
12CO CONCENTRATION (%)

FIG. 20

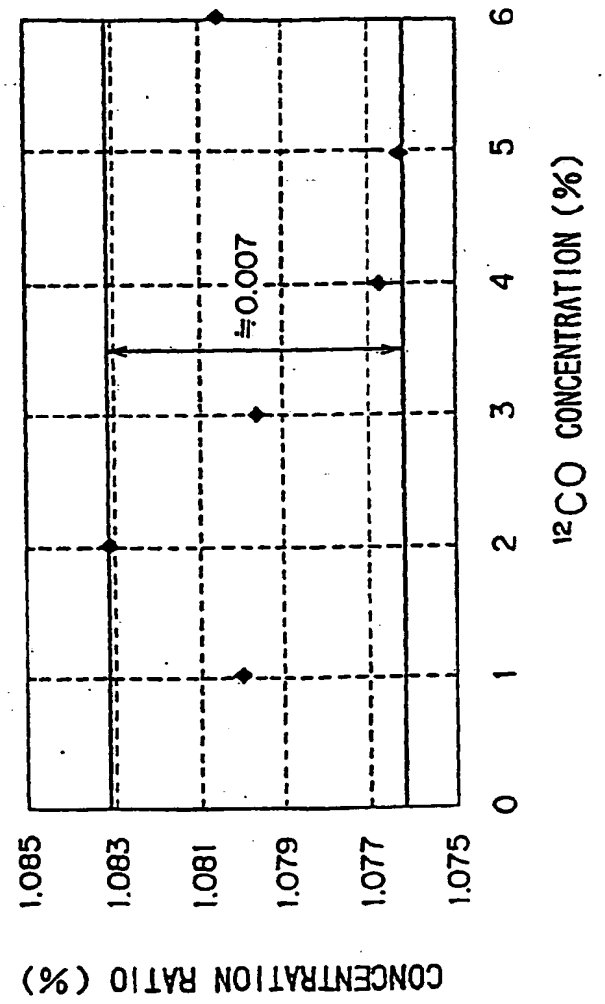

±0.007
0
1
2
3
4
5
6
^{12}CO CONCENTRATION (%)
1.085
1.083
1.081
1.079
1.077
1.075
CONCENTRATION RATIO (%)

FIG. 21

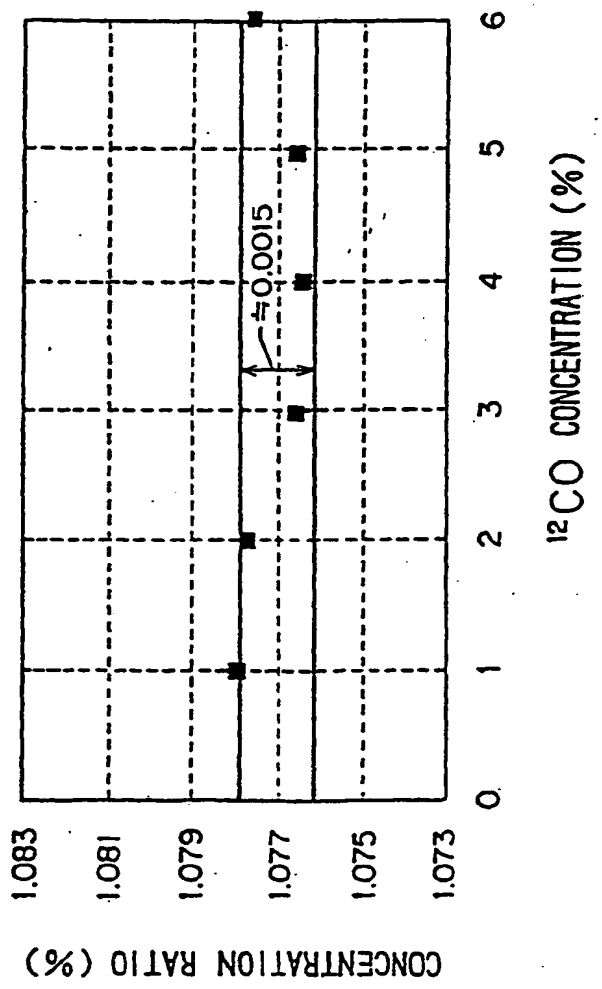

±0.0015
0
1
2
3
4
5
6
^{12}CO CONCENTRATION (%)
1.083
1.081
1.079
1.077
1.075
1.073
CONCENTRATION RATIO (%)

FIG. 22

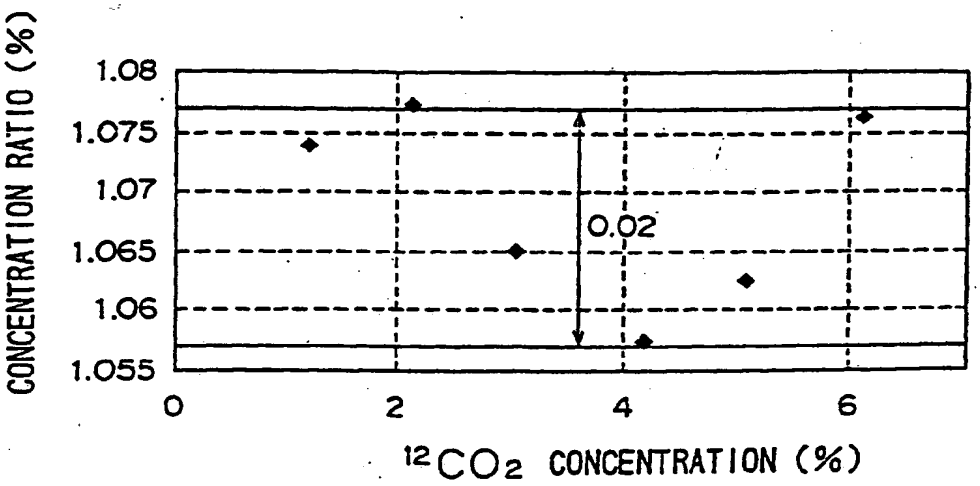

CONCENTRATION RATIO (%)
1.08
1.075
1.07
1.065
1.06
1.055
0.02
0
2
4
6
$^{12}CO_2$ CONCENTRATION (%)

FIG. 23

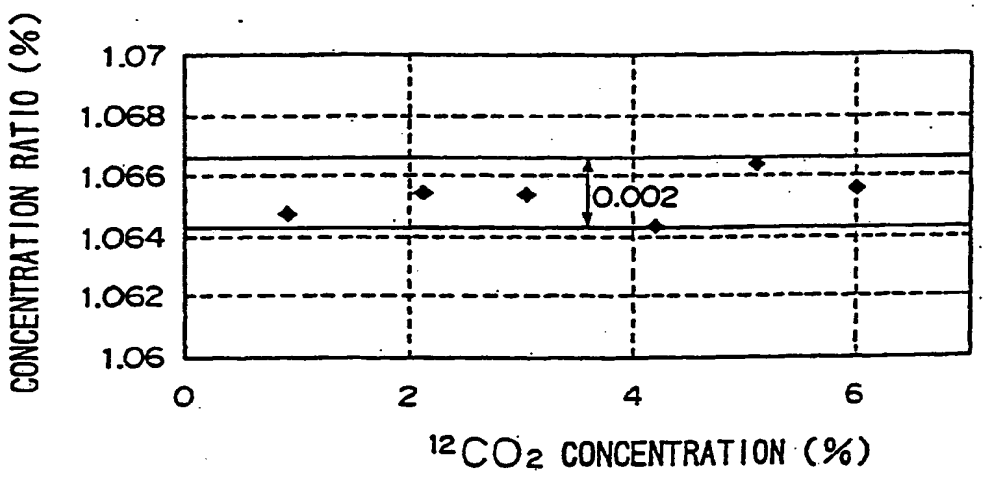
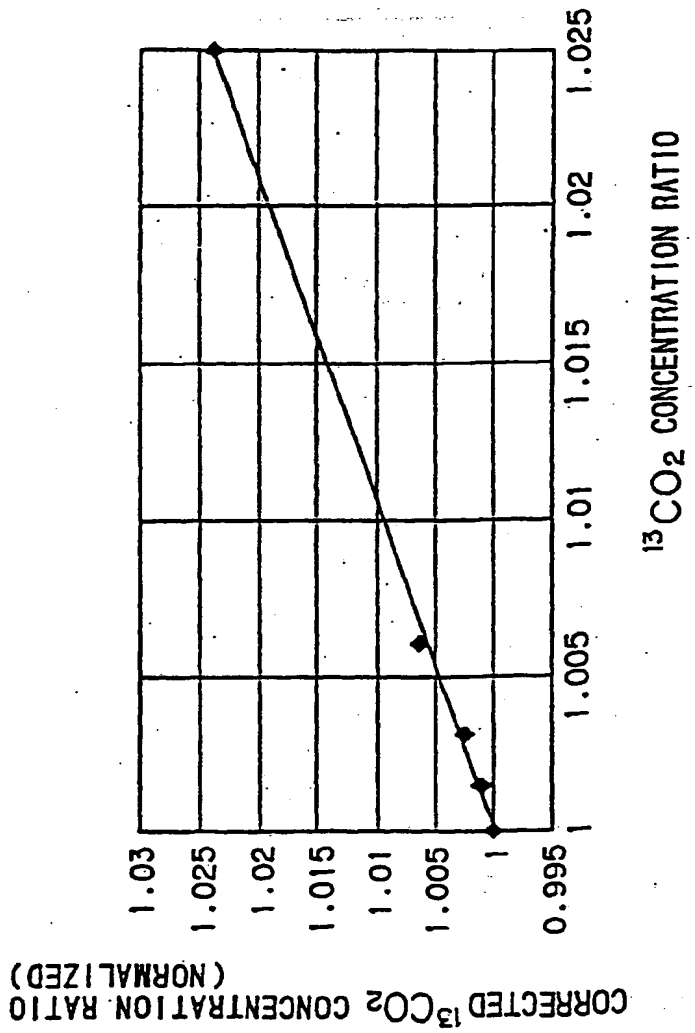

CONCENTRATION RATIO (%)
1.07
1.068
1.066
1.064
1.062
1.06
0.002
0
2
4
6
$^{12}CO_2$ CONCENTRATION (%)

FIG. 24


1.03
1.025
1.02
1.015
1.01
1.005
1
0.995
1
1.005
1.01
1.015
1.02
1.025
CORRECTED $^{13}CO_2$ CONCENTRATION RATIO (NORMALIZED)
$^{13}CO_2$ CONCENTRATION RATIO

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